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THERMOPLASTIC ARTICLES COMPRISING A FRINGED SURFACE STRUCTURE

FIELD OF THE INVENTION

5 This invention relates to an improved mono-layer or multi-layer film, sheet, or coating which comprises at least one layer which has or comprises a fringed surface microstructure. The invention also provides uses of such improved film, sheet or coating, as well as articles of manufacture made therefrom. Furthermore, the invention provides a new process to make a film, sheet or coating with a fringed surface microstructure.

10 BACKGROUND OF THE INVENTION

Plastic articles and items with a pleasant haptic appearance, such as a textile-like touch, and good optics are desirable for numerous applications, including hygienic products or garments. To improve aesthetics, for example of a plastic film, various techniques of surface modification have been employed, including, for example, extrusion under conditions favoring melt fracture, and embossing. Known surface modification processes to make solid 15 surface features, particularly filament-like structures, include use of a calender roll or belt having holes in the surface, peeling films with a melted layer from an adherent surface forming fibrils upon removal and electrostatic flocking.

According to U.S. Patent No. 5,814,413 surface-texturing of a polymer film is 20 accomplished by taking advantage of the usually undesired phenomenon of melt fracture. The patent discloses extruded films which due to melt fracture show a rough surface texture.

International Patent Application WO 99/16608 discloses a method for making an embossed oriented film. Said method discloses the steps of softening at least one of the two major surfaces of an oriented film, embossing the softened surface(s), and cooling the 25 resulting embossed oriented thermoplastic film. In order to maintain orientation the combined steps of softening, embossing and cooling should occur within a second.

International Patent Application WO 97/02128 provides a process for producing a surface-structured, sheet-like semi-finished product made from thermoplastic polymers. The resulting product is reported to have a velour-like or velvety surface with numerous solid 30 fibrous projections which can be longer than 3 millimeters. According to the disclosed process, the thermoplastic material is extruded in the molten state onto a moving belt or roller surface which is covered with cavities or borings having a depth of between 2 and 4 millimeters. The roller surface is exposed to a vacuum from the outside thus removing the air

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behavior indicating anti-slip properties. It is another object of the present invention to provide a surface-structured plastic article having increased heat resistance. It is yet another object of the present invention to provide a plastic article having enhanced storage, capturing or storing properties. It is yet another object of the present invention to provide a plastic article showing good water repellency.

It is a particular object of the present invention to provide a plastic article, which displays any desired combination of the above-mentioned properties, and may afford additional advantageous performance attributes depending on the intended end-use application or applications.

The objects of the present invention are achieved by providing a film, sheet, or coating, which is characterized by a distinct morphology. Such morphology is reflected in the presence of at least one layer having a fringed surface microstructure and, optionally, of further layers affording certain additional functions, for example, heat sealability, bulk or mechanical properties. The morphology and composition of the film, sheet or coating of the invention can be tailored to satisfy the particular requirements of the production process and the intended end-use application(s).

SUMMARY OF THE INVENTION

The present invention pertains to a mono-layer or multi-layer film, sheet, or coating. The film, sheet or coating of the invention comprises at least one layer which is a thermoplastic polymeric material and which is characterized by a fringed surface microstructure. The fringes are substantially solid fiber-like surface aberrations. The density of the fringes is at least 1000 per square centimeter, or higher. The layer is covered by the fringed microstructure on its entire surface, in one part, or in parts of its surface. The fringed surface microstructure may be discernible with the naked eye or on appropriate magnification. This includes a cured, irradiated or cross-linked film, sheet or coating, as well as a film, sheet, or coating comprising a cured, radiated or cross-linked material. The fringed layer may carry fringes on one or both (surface) sides, whether exposed (to the outside) or present as an interlayer surface.

In another aspect, the invention relates to a mono-layer or multi-layer foamed film, sheet or coating comprising a fringed microstructure.

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paper, glass, ceramic, cardboard, foil, wood or wood-based materials, such as particleboard or fiberboard, and metal, such as copper.

The term "multi-layer film, sheet, or coating " (including each individually e.g. "multi-layer film") as used herein indicates a film, sheet, or coating consisting of two, three, four, 5 five, six, seven or more layers.

The term "foamed film, sheet, or coating" (including each individually e.g. "foamed film") as used herein refers to a mono-layer or multi-layer structure wherein at least one layer of the structure is foamed and has a density less than the non-foamed layer or polymer.

10 The term "composite" as used herein refers to a multi-layer or multi-component article or material comprising at least one film, sheet, or coating layer having a fringed surface structure, (including, for example, but not limited to, a fabric or a laminated structure which may comprise, for example foil or paper).

The term "polymeric material" as used herein refers to a polymeric compound 15 obtainable by polymerizing one or more monomers. The generic term "polymeric compound" or "polymer" is intended to include a homopolymer, usually employed to refer to polymers prepared from only one monomer, and an interpolymer as defined hereinafter.

The term "comprising" as used herein means "including".

20 The term "interpolymer" as used herein refers to polymers prepared by the polymerization of at least two monomers. The generic term interpolymer thus embraces the terms copolymer, usually employed to refer to polymers prepared from two different monomers, and polymers prepared from more than two different monomers, such as terpolymers.

25 Unless specified otherwise, the term "alpha-olefin" (" α -olefin") as used herein refers to an aliphatic or cyclo-aliphatic alpha-olefin having at least 3, preferably 3 to 20 carbon atoms.

30 Unless indicated to the contrary, all parts, percentages and ratios are by weight. The expression "up to" when used to specify a numerical range includes any value less than or equal to the numerical value which follows this expression. The expressions "cc" or "ccm" stand for "cubic centimeters".

Thermoplastic Materials

The film, sheet, or coating of the invention is based on or made from one or more thermoplastic polymeric materials, including, for example, latex. Preferred thermoplastic
5 polymeric materials are semicrystalline polymers, amorphous polymers, or blends thereof. Advantageously, suitable thermoplastic polymers may be selected from the group consisting of polyolefins, poly(lactide), alkenyl aromatic polymers, thermoplastic polyurethanes, polycarbonates, polyamides, polyethers, thermoplastic phenoxy resins, polyvinyl chloride
10 polymers, polyvinylidene chloride polymers and polyesters, including certain elastomers and block polymers. Semicrystalline thermoplastic materials and blends thereof are preferred.

Suitable polyolefins include, for example, ethylene-based polymers, including ethylene homopolymer and interpolymer, aliphatic alpha-olefin homopolymers, such as polypropylene, polybutene and polyisoprene, and their interpolymers.

Ethylene homopolymers, for example low density polyethylene (LDPE) and high
15 density polyethylene (HDPE), and ethylene interpolymers are known classes of thermoplastic polymers, each having many members. They are prepared by homopolymerizing ethylene or interpolymerizing (for example, copolymerizing) ethylene with one or more vinyl- or diene-based comonomers, for example, α -olefins of 3 to about 20 carbon atoms, vinyl esters, vinyl acids, styrene-based monomers, monomers containing two
20 or more sites of ethylenic unsaturation, etc., using known copolymerization reactions and conditions.

Ethylene (based) polymers suitable for use in the present invention include both homogeneously branched (homogeneous) polymers and heterogeneously branched (heterogeneous) polymers.

25 "Homogeneous" polymers encompass ethylene-based interpolymers in which any comonomer is randomly distributed within a given interpolymer molecule and substantially all of the interpolymer molecules have the same ethylene/comonomer ratio within that interpolymer. Homogeneous ethylene polymers generally are characterized as having an essentially single melting (point) peak between -30°C and 150°C, as determined by
30 differential scanning calorimetry (DSC). The single melting peak may be relatively broad, such as is the case when an ethylene polymer having a crystallinity of less than about 36

percent is employed. The single melting peak may be sharp, such as is the case when an ethylene polymer having a crystallinity of at least about 36 percent is employed.

Typically, homogeneous ethylene polymers will also have a relatively narrow molecular weight distribution (MWD) as compared to corresponding heterogeneous ethylene polymers. Preferably, the molecular weight distribution defined as the ratio of weight average
5 molecular weight to number average molecular weight (M_w/M_n), is less than about 3.5 (when the density of the interpolymer is less than about 0.960 g/cc), more preferably less than about 3.0.

In addition or in the alternative, the homogeneity of the ethylene-based polymers is
10 reflected in a narrow composition distribution, which can be expressed using parameters such as SCBDI (Short Chain Branch Distribution Index) or (CDBI Composition Distribution Branch Index). The SCBDI of a polymer is readily calculated from data obtained from techniques known in the art, such as, for example, temperature rising elution fractionation (abbreviated herein as "TREF") as described, for example, in Wild et al, Journal of Polymer
15 Science, Poly. Phys. Ed., Vol. 20, p. 441 (1982), in U.S. Patent 4,798,081 (Hazlitt et al.), or in U.S. Patent 5,089,321 (Chum et al.), the disclosures of all of which are incorporated herein by reference. CDBI is defined as the weight percent of the polymer molecules having a comonomer content within 50 percent of the median total molar comonomer content. The SCBDI or CDBI for the homogeneous linear and substantially linear ethylene/alpha-olefin
20 polymers used in the present invention is typically greater than about 50 percent.

The homogeneous ethylene polymers that can be used in the present invention fall into two broad categories, the linear homogeneous ethylene polymers and the substantially linear homogeneous ethylene polymers. Both are known.

Homogeneous linear ethylene polymers have long been commercially available. As
25 exemplified in U.S. Patent No. 3,645,992 to Elston, homogeneous linear ethylene polymers can be prepared in conventional polymerization processes using Ziegler-type catalysts such as, for example, zirconium and vanadium catalyst systems. U.S. Patent No. 4,937,299 to Ewen et al. and U.S. Patent No. 5,218,071 to Tsutsui et al. disclose the use of metallocene catalysts, such as catalyst systems based on hafnium, for the preparation of homogeneous
30 linear ethylene polymers. Commercially available examples of homogeneous linear ethylene polymers include, for example, those sold by Mitsui Petrochemical Industries as TAFMER™ resins and by Exxon Chemical Company as EXACT™ and EXCEED™ resins.

The substantially linear ethylene polymers (SLEPs) are homogeneous polymers having long chain branching.

- The term "substantially linear ethylene polymer" as used herein means that the bulk ethylene polymer is substituted, on average, with about 0.01 long chain branches/1000 total carbons to about 3 long chain branches/1000 total carbons (wherein "total carbons" includes both backbone and branch carbon atoms). Preferred polymers are substituted with about 0.01 long chain branches/1000 total carbons to about 1 long chain branches/1000 total carbons, more preferably from about 0.05 long chain branches/1000 total carbons to about 1 long chain branches/1000 total carbons, and especially from about 0.3 long chain branches/1000 total carbons to about 1 long chain branches/1000 total carbons.

As used herein, the term "backbone" refers to a discrete molecule, and the term "polymer" or "bulk polymer" refers, in the conventional sense, to the polymer as formed in a reactor. For the polymer to be a "substantially linear ethylene polymer", the polymer must have at least enough molecules with long chain branching such that the average long chain branching in the bulk polymer is at least an average of from about 0.01/1000 total carbons to about 3 long chain branches/1000 total carbons.

The term "bulk polymer" as used herein means the polymer which results from the polymerization process as a mixture of polymer molecules and, for substantially linear ethylene polymers, includes molecules having an absence of long chain branching as well as molecules having long chain branching. Thus a "bulk polymer" includes all molecules formed during polymerization. It is understood that, for the substantially linear polymers, not all molecules have long chain branching, but a sufficient amount do such that the average long chain branching content of the bulk polymer positively affects the melt rheology (i.e., the melt fracture properties) as described herein below and elsewhere in the literature.

Long chain branching (LCB) is defined herein as a chain length of at least one (1) carbon (atom) less than the number of carbons in the comonomer, whereas short chain branching (SCB) is defined herein as a chain length of the same number of carbons in the residue of the comonomer after it is incorporated into the polymer molecule backbone. For example, a substantially linear ethylene/1-octene polymer has backbones with long chain branches of at least seven (7) carbons in length, but it also has short chain branches of only six (6) carbons in length.

Long chain branching can be distinguished from short chain branching by using ^{13}C nuclear magnetic resonance (NMR) spectroscopy and to a limited extent, e.g. for ethylene homopolymers, it can be quantified using the method of Randall, (Rev. Macromol.Chem. Phys., C29 (2&3), p. 285-297), the disclosure of which is incorporated herein by reference.

5 However as a practical matter, current ^{13}C nuclear magnetic resonance spectroscopy cannot determine the length of a long chain branch in excess of about six (6) carbon atoms and as such, this analytical technique cannot distinguish between a seven (7) carbon branch and a seventy (70) carbon branch. The long chain branch can be as long as about the same length as the length of the polymer backbone.

10 Although conventional ^{13}C nuclear magnetic resonance spectroscopy cannot determine the length of a long chain branch in excess of six carbon atoms, there are other known techniques useful for quantifying or determining the presence of long chain branches in ethylene polymers, including ethylene/1-octene interpolymers. For example, US Patent No. 4,500,648, incorporated herein by reference, teaches that long chain branching
15 frequency (LCB) can be represented by the equation $\text{LCB} = b/M_w$ wherein b is the weight average number of long chain branches per molecule and M_w is the weight average molecular weight. The molecular weight averages and the long chain branching characteristics are determined by gel permeation chromatography and intrinsic viscosity methods, respectively.

20 Two other useful methods for quantifying or determining the presence of long chain branches in ethylene polymers, including ethylene/1-octene interpolymers are gel permeation chromatography coupled with a low angle laser light scattering detector (GPC-LALLS) and gel permeation chromatography coupled with a differential viscometer detector (GPC-DV). The use of these techniques for long chain branch detection and the underlying
25 theories have been well documented in the literature. See, e.g., Zimm, G.H. and Stockmayer, W.H., J. Chem. Phys., 17, 1301 (1949) and Rudin, A., Modern Methods of Polymer Characterization, John Wiley & Sons, New York (1991) pp. 103-112, the disclosures of both of which are incorporated by reference.

A. Willem deGroot and P. Steve Chum, both of The Dow Chemical Company, at the
30 October 4, 1994 conference of the Federation of Analytical Chemistry and Spectroscopy Society (FACSS) in St. Louis, Missouri, presented data demonstrating that GPC-DV is indeed a useful technique for quantifying the presence of long chain branches in

substantially linear ethylene polymers. In particular, deGroot and Chum found that the level of long chain branches in substantially linear ethylene homopolymer samples measured using the Zimm-Stockmayer equation correlated well with the level of long chain branches measured using ^{13}C -NMR.

5 Further, deGroot and Chum found that the presence of octene does not change the hydrodynamic volume of the polyethylene samples in solution and, as such, one can account for the molecular weight increase attributable to octene short chain branches by knowing the mole percent octene in the sample. By deconvoluting the contribution to molecular weight increase attributable to 1-octene short chain branches, deGroot and Chum showed that
10 GPC-DV may be used to quantify the level of long chain branches in substantially linear ethylene/octene copolymers.

DeGroot and Chum also showed that a plot of $\log(I_2, \text{ melt index})$ as a function of $\log(\text{GPC Weight Average Molecular Weight})$ as determined by GPC-DV illustrates that the long chain branching aspects (but not the extent of long branching) of substantially linear
15 ethylene polymers are comparable to that of high pressure, highly branched low density polyethylene (LDPE) and are clearly distinct from ethylene polymers produced using Ziegler-type catalysts such as titanium complexes and ordinary homogeneous catalysts such as hafnium and vanadium complexes.

For substantially linear ethylene polymers, the empirical effect of the presence of long
20 chain branching is manifested as enhanced rheological properties which are quantified and expressed in terms of gas extrusion rheometry (GER) results and/or melt flow, I_{10}/I_2 , increases.

The substantially linear ethylene polymers suitable for the purpose of the present invention are a unique class of compounds that are further defined in US Patent No.
25 5,272,236, US Patent No. 5,278,272, and US Patent No. 5,665,800, each of which is incorporated herein by reference. SLEPs are available from The Dow Chemical Company as polymers made by the INSITETM Process and Catalyst Technology, such as AFFINITYTM polyolefin plastomers (POPs), and from DuPont Dow Elastomers, L.L.C. as ENGAGETM polyolefin elastomers (POEs).

30 Substantially linear ethylene polymers differ significantly from the class of polymers conventionally known as homogeneously branched linear ethylene polymers described above. As an important distinction, substantially linear ethylene polymers do not have a

linear polymer backbone in the conventional sense of the term "linear" as is the case for homogeneously branched linear ethylene polymers. Substantially linear ethylene polymers also differ significantly from the class of polymers known conventionally as heterogeneously branched traditional Ziegler polymerized linear ethylene interpolymers (for example, ultra low density polyethylene, linear low density polyethylene (LLDPE) or high density polyethylene (HDPE) made, for example, using the technique disclosed by Anderson et al. in US Patent No. 4,076,698, in that substantially linear ethylene interpolymers are homogeneously branched polymers; that is, substantially linear ethylene polymers have a SCBDI greater than or equal to 50 percent, preferably greater than or equal to 70 percent, more preferably greater than or equal to 90 percent. Substantially linear ethylene polymers also differ from the class of heterogeneously branched ethylene polymers in that substantially linear ethylene polymers are characterized as essentially lacking a measurable high density or crystalline polymer fraction as determined using a temperature rising elution fractionation technique.

The substantially linear ethylene polymer for use in the present invention can be characterized as having

(a) melt flow ratio, $I_{10}/I_2 \leq 5.63$,

(b) a molecular weight distribution, M_w/M_n , as determined by gel permeation chromatography and defined by the equation:

$(M_w/M_n) \leq (I_{10}/I_2) - 4.63$,

(c) a gas extrusion rheology such that the critical shear rate at onset of surface melt fracture for the substantially linear ethylene polymer is at least 50 percent greater than the critical shear rate at the onset of surface melt fracture for a linear ethylene polymer, wherein the substantially linear ethylene polymer and the linear ethylene polymer comprise the same comonomer or comonomers, the linear ethylene polymer has an I_2 and M_w/M_n within ten percent of the substantially linear ethylene polymer and wherein the respective critical shear rates of the substantially linear ethylene polymer and the linear ethylene polymer are measured at the same melt temperature using a gas extrusion rheometer,

(d) a single differential scanning calorimetry, DSC, melting peak between -30°C and 150°C, and

(e) a short chain branching distribution index greater than 50 percent.

Determination of the critical shear rate and critical shear stress in regards to melt fracture as well as other rheology properties such as "rheological processing index" (PI), is performed using a gas extrusion rheometer (GER). The gas extrusion rheometer is described by M. Shida, R.N. Shroff and L.V. Cancio in Polymer Engineering Science, Vol. 17, No. 11, p. 770 (1977) and in Rheometers for Molten Plastics by John Dealy, published by Van Nostrand Reinhold Co. (1982) on pp. 97-99, the disclosures of both of which are incorporated herein by reference.

The processing index (PI) is measured at a temperature of 190°C, at nitrogen pressure of 2500 psig using a 0.0296 inch (752 micrometers) diameter (preferably a 0.0143 inch diameter die for high flow polymers, e.g. 50 - 100 I₂ melt index or greater), 20:1 L/D die having an entrance angle of 180°. The GER processing index is calculated in millipoise units from the following equation:

$$PI = 2.15 \times 10^6 \text{ dyne/cm}^2 / (1000 \times \text{shear rate}),$$

wherein: $2.15 \times 10^6 \text{ dyne/cm}^2$ is the shear stress at 2500 psi, and the shear

rate is the shear rate at the wall as represented by the following equation:

$$32 Q' / (60 \text{ sec/min})(0.745)(\text{Diameter} \times 2.54 \text{ cm/in})^3, \text{ wherein:}$$

Q' is the extrusion rate (gms/min),

0.745 is the melt density of polyethylene (gm/cm^3), and

Diameter is the orifice diameter of the capillary (inches).

The PI is the apparent viscosity of a material measured at apparent shear stress of $2.15 \times 10^6 \text{ dyne/cm}^2$.

For substantially linear ethylene polymers, the PI is less than or equal to 70 percent of that of a conventional linear ethylene polymer having an I₂, M_w/M_n and density each within ten percent of the substantially linear ethylene polymer.

An apparent shear stress vs. apparent shear rate plot is used to identify the melt fracture phenomena over a range of nitrogen pressures from 5250 to 500 psig using the die or GER test apparatus previously described. According to Ramamurthy in Journal of Rheology, 30(2), 337-357, 1986, above a certain critical flow rate, the observed extrudate irregularities may be broadly classified into two main types: surface melt fracture and gross melt fracture.

Surface melt fracture occurs under apparently steady flow conditions and ranges in detail from loss of specular gloss to the more severe form of "sharkskin". In this disclosure, the onset of surface melt fracture is characterized at the beginning of losing extrudate gloss at which the surface roughness of extrudate can only be detected by 40x magnification. The critical shear rate at onset of surface melt fracture for the substantially linear ethylene polymers is at least 50 percent greater than the critical shear rate at the onset of surface melt fracture of a linear ethylene polymer having about the same I_2 and M_w/M_n . Preferably, the critical shear stress at onset of surface melt fracture for the substantially linear ethylene polymers of the invention is greater than about 2.8×10^6 dyne/cm².

Gross melt fracture occurs at unsteady flow conditions and ranges in detail from regular (alternating rough and smooth, helical, etc.) to random distortions. For commercial acceptability, (e.g., in blown film products), surface defects should be minimal, if not absent. The critical shear rate at onset of surface melt fracture (OSMF) and critical shear stress at onset of gross melt fracture (OGMF) will be used herein based on the changes of surface roughness and configurations of the extrudates extruded by a GER. For the substantially linear ethylene polymers used in the invention, the critical shear stress at onset of gross melt fracture is preferably greater than about 4×10^6 dyne/cm².

For the processing index determination and for the GER melt fracture determination, substantially linear ethylene polymers are tested without inorganic fillers and do not have more than 20 ppm aluminum catalyst residue. Preferably, however, for the processing index and melt fracture tests, substantially linear ethylene polymers do contain antioxidants such as phenols, hindered phenols, phosphites or phosphonites, preferably a combination of a phenol or hindered phenol and a phosphite or a phosphonite.

The molecular weight distributions of ethylene polymers are determined by gel permeation chromatography (GPC) on a Waters 150 °C high temperature chromatographic unit equipped with a differential refractometer and three columns of mixed porosity. The columns are supplied by Polymer Laboratories and are commonly packed with pore sizes of 10^3 , 10^4 , 10^5 and 10^6 Å. The solvent is 1,2,4-trichlorobenzene, from which about 0.3 percent by weight solutions of the samples are prepared for injection. The flow rate is about 1.0 milliliters/minute, unit operating temperature is about 140°C and the injection size is about 100 microliters.

The molecular weight determination with respect to the polymer backbone is deduced

by using narrow molecular weight distribution polystyrene standards (from Polymer Laboratories) in conjunction with their elution volumes. The equivalent polyethylene molecular weights are determined by using appropriate Mark-Houwink coefficients for polyethylene and polystyrene (as described by Williams and Ward in Journal of Polymer Science, Polymer Letters, Vol. 6, p. 621, 1968, the disclosure of which is incorporated herein
5 by reference) to derive the following equation:

$$M_{\text{polyethylene}} = a * (M_{\text{polystyrene}})^b.$$

In this equation, $a = 0.4316$ and $b = 1.0$. Weight average molecular weight, M_w , is calculated in the usual manner according to the following formula:

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$$M_j = (\sum w_i (M_i^j));$$

wherein w_i is the weight fraction of the molecules with molecular weight M_i eluting from the GPC column in fraction i and $j = 1$ when calculating M_w and $j = -1$ when calculating M_n .

Substantially linear ethylene polymers are known to have excellent processability,
15 despite having a relatively narrow molecular weight distribution (that is, the M_w/M_n ratio is typically less than about 3.5). Surprisingly, unlike homogeneously and heterogeneously branched linear ethylene polymers, the melt flow ratio (I_{10}/I_2) of substantially linear ethylene polymers can be varied essentially independently of the molecular weight distribution, M_w/M_n .

20 Suitable constrained geometry catalysts for manufacturing substantially linear ethylene polymers include constrained geometry catalysts as disclosed in U.S. application number 07/545,403, filed July 3, 1990; U.S. application number 07/758,654, filed September 12, 1991; U.S. Patent No. 5,132,380; U.S. Patent No. 5,064,802; U.S. Patent No. 5,470,993; U.S. Patent No. 5,453,410; U.S. Patent No. 5,374,696; U.S. Patent No. 5,532,394; U.S.
25 Patent No. 5,494,874; and U.S. Patent No. 5,189,192, the teachings of all of which are incorporated herein by reference.

Suitable catalyst complexes may also be prepared according to the teachings of WO 93/08199, and the patents issuing therefrom, all of which are incorporated herein by reference. Further, the monocyclopentadienyl transition metal olefin polymerization catalysts
30 taught in U.S. Patent No. 5,026,798, which is incorporated herein by reference, are also believed to be suitable for use in preparing the polymers of the present invention, so long as the polymerization conditions substantially conform to those described in US Patent No.

5,272,236; US Patent No. 5,278,272 and US Patent No. 5,665,800, especially with strict attention to the requirement of continuous polymerization. Such polymerization methods are also described in PCT/US 92/08812 (filed October 15, 1992).

The foregoing catalysts may be further described as comprising a metal coordination
5 complex comprising a metal of groups 3-10 or the Lanthanide series of the Periodic Table of the Elements and a delocalize β -bonded moiety substituted with a constrain-inducing moiety, said complex having a constrained geometry about the metal atom such that the angle at the metal between the centroid of the delocalized, substituted pi-bonded moiety and the center
10 of at least one remaining substituent is less than such angle in a similar complex containing a similar pi-bonded moiety lacking in such constrain-inducing substituent, and provided further that for such complexes comprising more than one delocalized, substituted pi-bonded moiety, only one thereof for each metal atom of the complex is a cyclic, delocalized, substituted pi-bonded moiety. The catalyst further comprises an activating cocatalyst.

Suitable cocatalysts for use herein include polymeric or oligomeric aluminoxanes,
15 especially methyl aluminoxane, as well as inert, compatible, noncoordinating, ion forming compounds. So called modified methyl aluminoxane (MMAO) is also suitable for use as a cocatalyst. One technique for preparing such modified aluminoxane is disclosed in US Patent No. 5,041,584, the disclosure of which is incorporated herein by reference. Aluminoxanes can also be made as disclosed in US Patent No. 5,218,071; US Patent No.
20 5,086,024; US Patent No. 5,041,585; US Patent No. 5,041,583; US Patent No. 5,015,749; US Patent No. 4,960,878; and US Patent No. 4,544,762, the disclosures of all of which are incorporated herein by reference.

Aluminoxanes, including modified methyl aluminoxanes, when used in the polymerization, are preferably used such that the catalyst residue remaining in the (finished)
25 polymer is preferably in the range of from about 0 to about 20 ppm aluminum, especially from about 0 to about 10 ppm aluminum, and more preferably from about 0 to about 5 ppm aluminum. In order to measure the bulk polymer properties (e.g. PI or melt fracture), aqueous HCl is used to extract the aluminoxane from the polymer. Preferred cocatalysts, however, are inert, noncoordinating, boron compounds such as those described in EP-A-
30 0520732, the disclosure of which is incorporated herein by reference.

Substantially linear ethylene are produced via a continuous (as opposed to a batch) controlled polymerization process using at least one reactor (e.g., as disclosed in WO

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Heterogeneous ethylene-based polymers encompass ethylene/ α -olefin interpolymers characterized as having a linear backbone and a DSC melting curve having a distinct melting point peak greater than 115°C attributable to a high density fraction. Such heterogeneous interpolymers will typically have a broader molecular weight distribution than homogeneous
5 interpolymers, as reflected in a M_w/M_n ratio of greater than about 3.5 (when the density of the interpolymers is less than about 0.960 g/cc). Typically, heterogeneous ethylene interpolymers have a CDBI of about 50 % or less, indicating that such interpolymers are a mixture of molecules having differing comonomer contents and differing amounts of short chain branching.

10 The heterogeneous ethylene polymers that can be used in the practice of this invention fall into two broad categories, those prepared with a free radical initiator at high temperature and high pressure, and those prepared with a coordination catalyst at high temperature and relatively low pressure. The former are generally known as low density polyethylenes (LDPE) and are characterized by branched chains of polymerized monomer
15 units pendant from the polymer backbone. LDPE polymers generally have a density between about 0.910 and 0.935 g/cc. Ethylene polymers and copolymers prepared by the use of a coordination catalyst, such as a Ziegler or Phillips catalyst, are generally known as linear polymers because of the substantial absence of branch chains of polymerized monomer units pendant from the backbone. High density polyethylene (HDPE), generally
20 having a density of about 0.941 to about 0.965 g/cc, is typically a homopolymer of ethylene, and it contains relatively few branch chains relative to the various linear copolymers of ethylene and an α -olefin. HDPE is well known, commercially available in various grades, and may be used in this invention.

Linear copolymers of ethylene and at least one α -olefin of 3 to 12 carbon atoms,
25 preferably of 4 to 8 carbon atoms, are also well known and commercially available. As is well known in the art, the density of a linear ethylene/ α -olefin copolymer is a function of both the length of the α -olefin and the amount of such monomer in the copolymer relative to the amount of ethylene, the greater the length of the α -olefin and the greater the amount of α -olefin present, the lower the density of the copolymer. Linear low density polyethylene
30 (LLDPE) is typically a copolymer of ethylene and an α -olefin of 3 to 12 carbon atoms, preferably 4 to 8 carbon atoms (for example, 1-butene, 1-octene, etc.), that has sufficient α -olefin content to reduce the density of the copolymer to that of LDPE. When the copolymer contains even more α -olefin, the density will drop below about 0.91 g/cc and these

- c) single ring alicyclic dienes such as 4-vinylcyclohexene, 1-allyl-4-isopropylidene cyclohexane, 3-allylcyclopentene, 4-allylcyclohexene, and 1-isopropenyl-4-butenylcyclohexane;
- d) multi-ring alicyclic fused and bridged ring dienes such as dicyclopentadiene; alkenyl, alkylidene, cycloalkenyl and cycloalkylidene norbornenes such as 5-methylene-2-norbornene, 5-methylene-6-methyl-2-norbornene, 5-methylene-6, 6-dimethyl-2-norbornene, 5-propenyl-2-norbornene, 5-(3-cyclopentenyl)-2-norbornene, 5-ethylidene-2-norbornene, 5-cyclohexylidene-2-norbornene, etc.

The preferred dienes are selected from the group consisting of 1,4-hexadiene, dicyclopentadiene, 5-ethylidene-2-norbornene, 5-methylene-2-norbornene, 7-methyl-1, 6-octadiene, piperylene, 4-vinylcyclohexene, etc.

The preferred terpolymers for the practice of the invention are terpolymers of ethylene, propylene and a non-conjugated diene (EPDM). Such terpolymers are commercially available. Ethylene/ α -olefin/diene terpolymers are useful when it is desired to make elastomeric polymer blends vulcanizable with the well known sulfur compound vulcanization process.

Ethylene/unsaturated carboxylic acid, salt and ester interpolymers may also be used in this invention. These are interpolymers of ethylene with at least one comonomer selected from the group consisting of vinyl esters of a saturated carboxylic acid wherein the acid moiety has up to 4 carbon atoms, unsaturated mono- or dicarboxylic acids of 3 to 5 carbon atoms, a salt of the unsaturated acid, esters of the unsaturated acid derived from an alcohol having 1 to 8 carbon atoms, and mixtures thereof. Terpolymers of ethylene and these comonomers are also suitable. Ionomers, which are completely or partially neutralized copolymers of ethylene and the acids described above, are discussed in more detail in U.S. Patent 3,264,272, already incorporated herein by reference. In addition, terpolymers of ethylene/vinyl acetate/carbon monoxide or ethylene/methyl acrylate/carbon monoxide containing up to about 15 percent by weight of carbon monoxide can also be employed.

Suitable ethylene/unsaturated carboxylic acid, salt and ester interpolymers include ethylene/vinyl acetate (EVA) including, but not limited to, the stabilized EVA described in U. S. Patent 5,096,955, which is incorporated herein by reference; ethylene/acrylic acid (EAA) and its ionomers; ethylene/methacrylic acid and its ionomers; ethylene/methyl acrylate; ethylene/ethyl acrylate; ethylene/isobutyl acrylate; ethylene/normal butyl acrylate;

ethylene/isobutyl acrylate/methacrylic acid and its ionomers; ethylene/normal butyl acrylate/methacrylic acid and its ionomers; ethylene/isobutyl acrylate/acrylic acid and its ionomers; ethylene/normal butyl acrylate/acrylic acid and its ionomers; ethylene/methyl methacrylate; ethylene/vinyl acetate/methacrylic acid and its ionomers; ethylene/vinyl acetate/acrylic acid and its ionomers; ethylene/vinyl acetate/carbon monoxide; ethylene/methacrylate/carbon monoxide; ethylene/normal butyl acrylate/carbon monoxide; ethylene/isobutyl acrylate/carbon monoxide; ethylene/vinyl acetate/monoethyl maleate and ethylene/methyl acrylate/monoethyl maleate. Particularly suitable copolymers are EVA; EAA; ethylene/methyl acrylate; ethylene/isobutyl acrylate; and ethylene/methyl methacrylate copolymers and mixtures thereof. Certain properties, such as tensile elongation, are taught to be improved by certain combinations of these ethylene interpolymers described in U. S. Patent 4,379,190, which is incorporated herein by reference. The procedures for making these ethylene interpolymers are well known in the art and many are commercially available.

Propylene based polymers are also suitable to make a film, sheet, or coating according to this invention. Such propylene based polymers are, for example, homopolypropylene and propylene interpolymers, such as copolymers of propylene with ethylene and/or a C₄-C₂₀ alpha-olefin, including impact copolymers and polypropylene random copolymers.

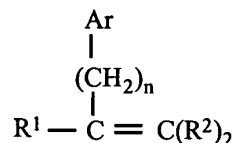
Further thermoplastic interpolymers suitable to practice the present invention are polyolefin interpolymers comprising

- i) polymer units derived from at least one of ethylene and/or an alpha-olefin monomer; and
- ii) polymer units derived from one or more vinyl or vinylidene aromatic monomers and/or one or more sterically hindered aliphatic or cycloaliphatic vinyl or vinylidene monomers, or a combination of at least one aromatic vinyl or vinylidene monomer, and
- iii) optionally polymer units derived from one or more ethylenically unsaturated polymerizable monomer(s) other than those derived from i) and ii).

Suitable α -olefins include, for example, α -olefins containing from 3 to about 20, preferably from 3 to about 12, more preferably from 3 to about 8 carbon atoms. These α -olefins do not contain an aromatic moiety. Particularly suitable are ethylene, propylene, butene-1, 4-methyl-1-pentene, hexene-1 or octene-1 or ethylene in combination with one or more of propylene, butene-1, 4-methyl-1-pentene, hexene-1 or octene-1.

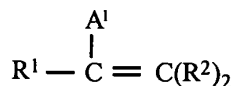
Polymerizable ethylenically unsaturated monomer(s) include strained ring olefins such as norbornene and C₁-C₁₀ alkyl or C₆-C₁₀ aryl substituted norbornenes, with an exemplary interpolymer being ethylene/styrene/norbornene.

Suitable vinyl or vinylidene aromatic monomers include, for example, those
 5 represented by the following formula:



wherein R¹ is selected from the group of radicals consisting of hydrogen and alkyl radicals containing from 1 to about 4 carbon atoms, preferably hydrogen or methyl; each R² is
 10 independently selected from the group of radicals consisting of hydrogen and alkyl radicals containing from 1 to about 4 carbon atoms, preferably hydrogen or methyl; Ar is a phenyl group or a phenyl group substituted with from 1 to 5 substituents selected from the group consisting of halo, C₁-C₄-alkyl, and C₁-C₄-haloalkyl; and n has a value from zero to about 4, preferably from zero to 2, most preferably zero. Exemplary vinyl aromatic monomers
 15 include styrene, vinyl toluene, α-methylstyrene, t-butyl styrene, chlorostyrene, including all isomers of these compounds, and the like. Particularly suitable such monomers include styrene and lower alkyl- or halogen-substituted derivatives thereof. Preferred monomers include styrene, α-methyl styrene, the lower alkyl-(C₁-C₄) or phenyl-ring substituted derivatives of styrene, such as for example, ortho-, meta-, and para-methylstyrene, the ring
 20 halogenated styrenes, para-vinyl toluene or mixtures thereof, and the like. The most preferred aromatic vinyl monomer is styrene.

By the term "sterically hindered aliphatic or cycloaliphatic vinyl or vinylidene compounds", it is meant addition polymerizable vinyl or vinylidene monomers corresponding to the formula:



wherein A¹ is a sterically bulky, aliphatic or cycloaliphatic substituent of up to 20 carbons, R¹ is selected from the group of radicals consisting of hydrogen and alkyl radicals containing from 1 to about 4 carbon atoms, preferably hydrogen or methyl; each R² is
 30 independently selected from the group of radicals consisting of hydrogen and alkyl radicals

containing from 1 to about 4 carbon atoms, preferably hydrogen or methyl; or alternatively R¹ and A¹ together form a ring system.

By the term "sterically bulky" it is meant that the monomer bearing this substituent is normally incapable of addition polymerization by standard Ziegler-Natta polymerization catalysts at a rate comparable with ethylene polymerizations.

Ethylene and alpha-olefins having a linear aliphatic structure such as propylene, butene-1, hexene-1 and octene-1 are not considered to be sterically hindered aliphatic monomers.

Preferred sterically hindered aliphatic or cycloaliphatic vinyl or vinylidene compounds are monomers in which one of the carbon atoms bearing ethylenic unsaturation is tertiary or quaternarily substituted. Examples of such substituents include cyclic aliphatic groups such as cyclohexyl, cyclohexenyl, cyclooctenyl, or ring alkyl or aryl substituted derivatives thereof, tert-butyl, norbornyl, and the like. Most preferred aliphatic or cycloaliphatic vinyl or vinylidene compounds are the various isomeric vinyl-ring substituted derivatives of cyclohexene and substituted cyclohexenes, and 5-ethylidene-2-norbornene. Especially suitable are 1-, 3-, and 4-vinylcyclohexene. Simple linear non-branched α -olefins including for example, α -olefins containing from 3 to about 20 carbon atoms such as propylene, butene-1, 4-methyl-1-pentene, hexene-1 or octene-1 are not examples of sterically hindered aliphatic or cycloaliphatic vinyl or vinylidene compounds.

The interpolymers comprising polymer units defined above under i), ii) and iii) can be substantially random, pseudo-random, random, alternating, diadic, triadic, tetradic or any combination thereof. That is, the interpolymer product can be variably incorporated and optionally variably sequenced. The preferred sequence is substantially random. The preferred substantially random interpolymers are the so-called pseudo-random interpolymers as described in EP-A-0 416 815 by James C. Stevens et al. and US Patent No. 5,703,187 by Francis J. Timmers, both of which are incorporated herein by reference in their entirety.

The preferred polyolefin interpolymer are ethylene/styrene interpolymers. Particularly preferred are substantially random ethylene/styrene interpolymers.

The term "variably incorporated" as used herein refers to an interpolymer, particularly an ethylene/styrene interpolymer, manufactured using at least two catalyst systems wherein during interpolymerization the catalyst systems are operated at different incorporation or reactivity rates. For example, the interpolymer product having a total styrene content of 36

weight percent is variably incorporated where one catalyst system incorporates 22 weight percent styrene and the other catalyst system incorporates 48 weight percent styrene and the production split between the two catalyst systems is 47/53 weight percentages.

Representative "pseudo-random" interpolymers are the ethylene/styrene
5 interpolymers described in U.S. Patent 5,703,187, the disclosure of which is incorporated herein in its entirety by reference.

"Random" interpolymers are those in which the monomer units are incorporated into the chain such that there exist various combinations of ordering including blockiness, e.g. where either the ethylene or the aliphatic alpha-olefin monomer or the sterically hindered
10 vinylidene monomer or both can be repeated adjacent to one another.

Representative "alternating" interpolymers are, for example, alternating ethylene/styrene interpolymers in which the ethylene and the sterically hindered vinylidene monomer occur in repeat alternate sequences on the polymer chain in atactic or stereospecific structures (such as isotactic or syndiotactic) or in combinations of the general
15 formula $(AB)_n$.

The term "substantially random" as used herein in reference to the interpolymers comprising the above-mentioned monomers i), ii) and iii), and to ethylene/ styrene interpolymers in particular, generally means that the distribution of the monomers of the interpolpolymer can be described by the Bernoulli statistical model or by a first or second order
20 Markovian statistical model, as described by J. C. Randall in Polymer Sequence Determination, Carbon-13 NMR Method, Academic Press New York, 1977, pp. 71-78, the disclosure of which is incorporated herein by reference. Substantially random interpolymers do not contain more than 15 mole percent of the total amount of vinyl or vinylidene aromatic monomer in blocks of vinyl or vinylidene aromatic monomer of more than 3 units.

25 Preferably, the substantially random interpolpolymer is not characterized by a high degree (greater than 50 mole percent) of either isotacticity or syndiotacticity. This means that in the carbon-13 NMR spectrum of the substantially random interpolpolymer, the peak areas corresponding to the main chain methylene and methine carbons representing either meso diad sequences or racemic diad sequences should not exceed 75 percent of the total
30 peak area of the main chain methylene and methine carbons.

A preferred method of preparation of the substantially random interpolymers includes polymerizing a mixture of polymerizable monomers in the presence of one or more

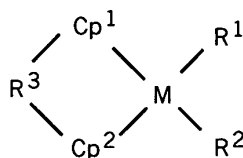
metallocene or constrained geometry catalysts in combination with various cocatalysts, as described in EP-A-0,416,815 by James C. Stevens et al. and US Patent No. 5,703,187 by Francis J. Timmers, both of which are incorporated herein by reference in their entirety.

5 Preferred operating conditions for such polymerization reactions are pressures from atmospheric up to 3000 atmospheres and temperatures from -30°C to 200°C.

Polymerizations and unreacted monomer removal at temperatures above the autopolymerization temperature of the respective monomers may result in formation of some amounts of homopolymer polymerization products resulting from free radical polymerization.

10 Examples of suitable catalysts and methods for preparing the substantially random interpolymers are disclosed in EP-A-514,828); as well as U.S. Patents: 5,055,438; 5,057,475; 5,096,867; 5,064,802; 5,132,380; 5,189,192; 5,321,106; 5,347,024; 5,350,723; 5,374,696; 5,399,635; 5,470,993; 5,703,187; and 5,721,185, all of which patents and applications are incorporated herein by reference.

15 The substantially random α -olefin/vinyl aromatic interpolymers can also be prepared by the methods described in JP 07/278230 employing compounds shown by the general formula



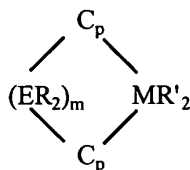
20 wherein Cp¹ and Cp² are cyclopentadienyl groups, indenyl groups, fluorenyl groups, or substituents of these, independently of each other; R¹ and R² are hydrogen atoms, halogen atoms, hydrocarbon groups with carbon numbers of 1-12, alkoxy groups, or aryloxy groups, independently of each other; m is a group IV metal, preferably Zr or Hf, most preferably Zr; and R³ is an alkylene group or silanediyl group used to cross-link Cp¹ and Cp².

25 The substantially random α -olefin/vinyl aromatic interpolymers can also be prepared by the methods described by John G. Bradfute et al. (W. R. Grace & Co.) in WO 95/32095; by R. B. Pannell (Exxon Chemical Patents, Inc.) in WO 94/00500; and in Plastics Technology, p. 25 (September 1992), all of which are incorporated herein by reference in their entirety.

Also suitable are the substantially random interpolymers which comprise at least one α -olefin/vinyl aromatic/vinyl aromatic/ α -olefin tetrad disclosed in U.S. Application No. 08/708,869 filed September 4, 1996 and WO 98/09999 both by Francis J. Timmers et al.. These interpolymers contain additional signals in their carbon-13 NMR spectra with intensities greater than three times the peak to peak noise. These signals appear in the chemical shift ranges of 43.70 - 44.25 ppm and 38.0 - 38.5 ppm. Specifically, major peaks are observed at 44.1, 43.9, and 38.2 ppm. A proton test NMR experiment indicates that the signals in the chemical shift region 43.70 - 44.25 ppm are methine carbons and the signals in the region 38.0 - 38.5 ppm are methylene carbons.

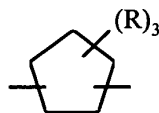
It is believed that these new signals are due to sequences involving two head-to-tail vinyl aromatic monomer insertions preceded and followed by at least one α -olefin insertion, e.g. an ethylene/styrene/styrene/ethylene tetrad wherein the styrene monomer insertions of said tetrads occur exclusively in a 1,2 (head to tail) manner. It is understood by one skilled in the art that for such tetrads involving a vinyl aromatic monomer other than styrene and an α -olefin other than ethylene that the ethylene/vinyl aromatic monomer/vinyl aromatic monomer/ethylene tetrad will give rise to similar carbon-13 NMR peaks but with slightly different chemical shifts.

These interpolymers can be prepared by conducting the polymerization at temperatures of from about -30°C to about 250°C in the presence of such catalysts as those represented by the formula



wherein: each C_p is independently, each occurrence, a substituted cyclopentadienyl group π -bound to M; E is carbon or Si; M is a group IV metal, preferably Zr or Hf, most preferably Zr; each R is independently, each occurrence, hydrogen, hydrocarbyl, silahydrocarbyl, or hydrocarbylsilyl, containing up to about 30 preferably from 1 to about 20 more preferably from 1 to about 10 carbon or silicon atoms; each R' is independently, each occurrence, hydrogen, halo, hydrocarbyl, hydrocarbyloxy, silahydrocarbyl, hydrocarbylsilyl containing up to about 30, preferably from 1 to about 20, more preferably from 1 to about 10 carbon or silicon atoms or two R' groups together can be a C_1 - C_{10} hydrocarbyl substituted 1,3-

butadiene; M is 1 or 2; and optionally, but preferably in the presence of an activating cocatalyst. Particularly, suitable substituted cyclopentadienyl groups include those illustrated by the formula:



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wherein each R is independently, each occurrence, hydrogen, hydrocarbyl, silahydrocarbyl, or hydrocarbylsilyl, containing up to about 30, preferably from 1 to about 20, more preferably from 1 to about 10 carbon or silicon atoms or two R groups together form a divalent derivative of such group. Preferably, R independently each occurrence is (including where appropriate all isomers) hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, benzyl, phenyl or silyl or (where appropriate) two such R groups are linked together forming a fused ring system such as indenyl, fluorenyl, tetrahydroindenyl, tetrahydrofluorenyl, or octahydrofluorenyl.

15 Particularly preferred catalysts include, for example, racemic-(dimethylsilanediyl)-bis-(2-methyl-4-phenylindenyl) zirconium dichloride, racemic-(dimethylsilanediyl)-bis-(2-methyl-4-phenylindenyl) zirconium 1,4-diphenyl-1,3-butadiene, racemic-(dimethylsilanediyl)-bis-(2-methyl-4-phenylindenyl) zirconium di-C₁₋₄ alkyl, racemic-(dimethylsilanediyl)-bis-(2-methyl-4-phenylindenyl) zirconium di-C₁-C₄ alkoxide, or any combination thereof and the like.

20 It is also possible to use the following titanium-based constrained geometry catalysts, [N-(1,1-dimethylethyl)-1,1-dimethyl-1-[(1,2,3,4,5-η)-1,5,6,7-tetrahydro-s-indacen-1-yl]silanaminato(2-)-N]titanium dimethyl; (1-indenyl)(tert-butylamido)dimethylsilane titanium dimethyl; ((3-tert-butyl)(1,2,3,4,5-η)-1-indenyl)(tert-butylamido) dimethylsilane titanium dimethyl; and ((3-iso-propyl)(1,2,3,4,5-η)-1-indenyl)(tert-butyl amido)dimethylsilane titanium dimethyl, or any combination thereof and the like.

Further preparative methods for the interpolymers used in the present invention have been described in the literature. Longo and Grassi (Makromol. Chem., Volume 191, pages 2387 to 2396 [1990]) and D'Anniello et al. (Journal of Applied Polymer Science, Volume 58, pages 1701-1706 [1995]) reported the use of a catalytic system based on methylalumoxane (MAO) and cyclopentadienyltitanium trichloride (CpTiCl₃) to prepare an ethylene-styrene copolymer. Xu and Lin (Polymer Preprints, Am. Chem. Soc., Div. Polym. Chem., Vol. 35,

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pages 686-687 [1994]) have reported copolymerization using a $\text{MgCl}_2/\text{TiCl}_4/\text{NdCl}_3/\text{Al}(\text{iBu})_3$ catalyst to give random copolymers of styrene and propylene. Lu et al. (Journal of Applied Polymer Science, Vol. 53, pp. 1453 to 1460, 1994) have described the copolymerization of ethylene and styrene using a $\text{TiCl}_4/\text{NdCl}_3/\text{MgCl}_2/\text{Al}(\text{Et})_3$ catalyst. Sernetz and Mulhaupt,
5 (Macromol. Chem. Phys., Vol. 197, pp. 1071-1083, 1997) have described the influence of polymerization conditions on the copolymerization of styrene with ethylene using $\text{Me}_2\text{Si}(\text{Me}_4\text{Cp})(\text{n-tert-butyl})\text{TiCl}_2/\text{methylaluminumoxane}$ Ziegler-Natta catalysts. Copolymers of ethylene and styrene produced by bridged metallocene catalysts have been described by Arai, Toshiaki and Suzuki (Polymer Preprints, Am. Chem. Soc., Div. Polym. Chem., Volume
10 38, pages 349-350, 1997; U.S. Patent No. 5,883,213 and DE-A-197 11 339) and in U.S. Patent No. 5,652,315, issued to Mitsui Toatsu Chemicals, Inc.. The manufacture of α -olefin/vinyl aromatic monomer interpolymers such as propylene/styrene and butene/styrene is as described in US Patent No. 5,244,996, issued to Mitsui Petrochemical Industries Ltd. or US Patent No. 5,652,315 also issued to Mitsui Petrochemical Industries Ltd, or as disclosed
15 in DE-A-197 11 339 to Denki Kagaku Kogyo KK. All the above methods disclosed for preparing the interpolymer component are incorporated herein by reference. Also, although of high isotacticity and therefore not "substantially random", the random copolymers of ethylene and styrene as disclosed in Polymer Preprints Vol. 39, No. 1, March 1998 by Toru Aria et al. can also be employed for the purposes of the present invention.

20 While preparing the substantially random interpolymer, an amount of atactic vinyl aromatic homopolymer may be formed due to homopolymerization of the vinyl aromatic monomer at elevated temperatures. The presence of vinyl aromatic homopolymer is in general not detrimental for the purposes of the present invention and can be tolerated.

The substantially random interpolymer usually contains from about 5 to about 65,
25 preferably from about 5 to about 55, more preferably from about 10 to about 50 mole percent of at least one vinyl or vinylidene aromatic monomer; or sterically hindered aliphatic or cycloaliphatic vinyl or vinylidene monomer; or both; and from about 35 to about 95, preferably from about 45 to about 95, more preferably from about 50 to about 90 mole percent of ethylene and/or at least one aliphatic α -olefin having from about 3 to about 20
30 carbon atoms.

The most preferred substantially random interpolymers are interpolymers of ethylene and styrene and interpolymers of ethylene, styrene and at least one alpha-olefin containing from 3 to 8 carbon atoms.

The presence of other polymerizable ethylenically unsaturated monomer(s) is optional.

The density of the substantially random interpolymer is generally about 0.930 g/cm³ or more, preferably from about 0.930 to about 1.045 g/cm³, more preferably from about 0.930 to about 1.040 g/cm³, most preferably from about 0.930 to about 1.030 g/cm³. The molecular weight distribution, M_w/M_n , is generally from about 1.5 to about 20, preferably from about 1.8 to about 10, more preferably from about 2 to about 5.

Thermoplastic polymers useful in the present invention also include alkenyl aromatic polymers. The alkenyl aromatic polymers may be comprised solely of one or more alkenyl aromatic homopolymers, one or more alkenyl aromatic copolymers, a blend of one or more of each of alkenyl aromatic homopolymers and copolymers, or blends of any of the foregoing with a non-alkenyl aromatic polymer. Regardless of composition, the alkenyl aromatic polymer material comprises greater than 50 weight percent and preferably greater than 70 weight percent alkenyl aromatic monomeric units. Most preferably, the alkenyl aromatic polymer material is comprised entirely of alkenyl aromatic monomeric units.

Suitable alkenyl aromatic polymers include homopolymers and copolymers derived from alkenyl aromatic compounds such as styrene, alpha-methylstyrene, ethylstyrene, vinyl benzene, vinyl toluene, chlorostyrene, and bromostyrene, t-butyl styrene, including all isomers of these compounds. Suitable polymers also include alkenyl aromatic polymers having a high degree of syndiotactic configuration. A preferred alkenyl aromatic polymer is polystyrene. Minor amounts of monoethylenically unsaturated compounds such as C₂-C₆ alkyl acids and esters, ionomeric derivatives, and C₄-C₆ dienes may be copolymerized with alkenyl aromatic compounds. Examples of copolymerizable compounds include acrylic acid, methacrylic acid, ethacrylic acid, maleic acid, itaconic acid, acrylonitrile, maleic anhydride, methyl acrylate, ethyl acrylate, isobutyl acrylate, n-butyl acrylate, methyl methacrylate, vinyl acetate and butadiene.

General purpose polystyrene is the most preferred alkenyl aromatic polymer material. The term "general purpose polystyrene" is defined in the Encyclopedia of Polymer Science and Engineering, Vol. 16, pp. 62-71, 1989. Such polystyrene is often called also referred to as crystal polystyrene or polystyrene homopolymer.

The monoalkenyl aromatic polymers may be suitably modified by rubbers to improve their impact properties. Examples of suitable rubbers are homopolymers of C₄-C₆ conjugated

dienes, especially butadiene or isoprene; interpolymers of one or more alkenyl aromatic monomers, and one or more C₄-C₆ conjugated dienes; interpolymers of ethylene and propylene or ethylene, propylene and a nonconjugated diene, especially 1,6-hexadiene or ethylidene norbornene; homopolymers of C₄-C₆ alkyl acrylates; interpolymers of C₄-C₆ alkyl acrylates and an interpolymizable comonomer, especially an alkenyl aromatic monomer or a C₁-C₄ alkyl methacrylate. Also included are graft polymers of the foregoing rubbery polymers wherein the graft polymer is an alkenyl aromatic polymer. A preferred alkenyl aromatic polymer for use in all of the foregoing rubbery polymers is styrene. A most preferred rubbery polymer is polybutadiene or a styrene/butadiene copolymer.

10 Impact modified alkenyl aromatic polymers are well known in the art and commercially available.

Suitable polymers to be employed as Component (A) also include alkenyl aromatic polymers having a high degree of syndiotactic configuration.

15 Preferred alkenyl aromatic polymers include polystyrene, syndiotactic polystyrene, rubber-modified high impact polystyrene, poly(vinyl-toluene), and poly(alpha-methylstyrene).

20 Thermoplastic polymers for use in the present invention also include melt-stable lactide polymers or poly(lactide). By "melt-stable" it is meant that the lactide polymer when subjected to melt-processing techniques adequately maintains its physical properties and does not generate by-products in sufficient quantity to foul or coat processing equipment. Lactide polymers are obtainable from lactic acid and may therefore also be referred to as PLA resins. Such lactide polymers are disclosed, for example, in US Patent No. 5,773,562, the disclosure of which is incorporated herein by reference in its entirety. Suitable PLA resins are supplied commercially by Cargill Dow under the designation EcoPLA. Poly(lactide) offers
25 the benefits of being a renewable resource material which may be obtained from corn and of being biodegradable (compostable). Thus, poly(lactide) may be disposed of in an environmentally sound fashion.

30 The poly(lactide) formulation may include a plasticizer. Suitable plasticizers and selection criteria are disclosed in US Patent No. 5,773,562 (column 14, line 35 – column 15, line 28).

To improve certain properties of poly(lactide) it may be advantageous to blend a second polymer with the poly(lactide). Suitable 'second polymers' and selection criteria are disclosed in US Patent No. 5,773,562 (column 7, lines 21-47).

Suitable elastomers and block polymers include, for example, block copolymers such as styrene/butadiene (SB) block copolymers, styrene/ethylene-butene/styrene (SEBS) block polymers, styrene/ethylene-propylene/styrene (SEPS) block polymers, styrene/isoprene/styrene (SIS) block polymers, and styrene/butadiene/styrene (SBS) block polymers; polyester/polyether block polymers (e.g., HYTEL™); ethylene/propylene rubbers; and ethylene/propylene/diene (EPDM) elastomers. Preferred elastomers are vinyl aromatic/conjugated diene block polymers (e.g. SBS) that have been substantially hydrogenated; that is the block copolymer is characterized by each hydrogenated vinyl aromatic polymer block having a hydrogenation level of greater than 90 percent and each hydrogenated conjugated diene polymer block having a hydrogenation level of greater than 95 percent where hydrogenation converts unsaturated moieties into saturated moieties. Also, preferred block polymers have a higher ratio of rigid polymer blocks (e.g. vinyl aromatic polymer blocks) to rubber polymer blocks (e.g. conjugated diene polymer blocks).

Suitable thermoplastic phenoxy resins include polyhydroxyaminoether, polyhydroxyesterether or polyhydroxyether.

The polymers used in the present invention may be modified, for example, but not limited to, by typical grafting, hydrogenation, functionalizing, or other reactions well known to those skilled in the art.

The graft modification of polymers, particularly polyolefins, such as polyethylenes and polypropylenes, with various unsaturated monomers is well known in the art. Such a modification renders an essentially nonpolar material compatible, at least to some limited extent, with a polar material. Graft modification of the polymers is advantageously accomplished by employing an organic compound containing at least one ethylenic unsaturation (e.g., at least one double bond), and at least one carbonyl group ($-C=O$). Representative of compounds that contain at least one carbonyl group are the carboxylic acids, anhydrides, esters and their salts, both metallic and nonmetallic. Preferably, the organic compound contains ethylenic unsaturation conjugated with a carbonyl group. Representative compounds include maleic, fumaric, acrylic, methacrylic, itatonic, crotonic, methyl crotonic and cinnamic acid and their anhydride, ester and salt derivatives, if any.

Maleic anhydride is the preferred unsaturated organic compound containing at least one ethylenic unsaturation and at least one carbonyl group.

5 The unsaturated organic compound content of the grafted polymer is at least about 0.01 weight percent, and preferably at least about 0.05 weight percent, based on the combined weight of the polymer and the organic compound. The maximum amount of unsaturated organic compound content can vary to convenience, but typically it does not exceed about 10 weight percent, preferably it does not exceed about 5 weight percent, and more preferably it does not exceed about 2 weight percent. The unsaturated organic compound can be grafted to the polymer by any known technique. The graft-modified
10 polymer may be blended with one or more other polymers, either grafted or ungrafted. For example, a graft modified ethylene-based or propylene-based polymer may be blended with one or more other polyolefins, either grafted or ungrafted, or with one or more polymers other than a polyolefin, either grafted or ungrafted.

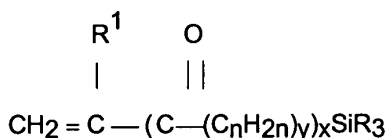
The polymers may be sulfonated or chlorinated to provide functionalized derivatives
15 according to established techniques. In addition or alternatively, the polymers may be modified by suitable chain-extending or cross-linking processes using e.g. a physical or a chemical method, including, but not limited to, peroxide-, silane-, sulfur-, radiation-, or azide-based cure systems. A more detailed description of the various cross-linking technologies is described in U.S. Patent No. 5,869,591 and EP-A-778,852, the entire contents of both of
20 which are herein incorporated by reference. Dual cure systems, which use a combination of heat, moisture cure and radiation steps, may be effectively employed. Dual cure systems are disclosed, for example, in EP-A-0 852 596, incorporated herein by reference. For instance, it may be desirable to employ peroxide crosslinking agents in conjunction with radiation, and sulfur-containing crosslinking agents in conjunction with silane crosslinking agents.

25 The present invention also provides a film, sheet, or coating, wherein the film, sheet, or coating, the thermoplastic polymeric material or both have been cured, irradiated, or crosslinked. Preferably, the cured, irradiated or crosslinked thermoplastic polymer is a polyolefin, more preferably a polyolefin as defined above, and most preferably an ethylene-based polymer. As used herein, "crosslinking" and "crosslinked" include partially
30 crosslinking (crosslinked) as well as fully crosslinking (crosslinked), as long as the crosslinking results in a gel which is verifiable via ASTM D2765, Procedure A. The various cross-linking agents can be used alone, or in combination with one another.

Suitable heat-activated cross-linking agents include free radical initiators, preferably organic peroxides, more preferably those with one hour half lives at temperatures greater than 120°C. For example, suitable cross-linking agents are organic peroxides, such as 1,1-di-t-butyl peroxy-3,3,5-trimethylcyclohexane, dicumyl peroxide, 2,5-dimethyl-2,5-di(t-butyl peroxy) hexane, t-butyl-cumyl peroxide, α,α' -di(butyl peroxy)-diisopropyl benzene, di-t-butyl peroxide, and 2,5-dimethyl- 2,5-di-(t-butyl peroxy) hexyne. Dicumyl peroxide is the preferred agent. Additional teachings to organic peroxide cross-linking agents are seen in C.P. Park, *Supra*, pp. 198-204, which is incorporated herein by reference.

Alternatively, polymers may be crosslinked or cured by first grafting a silane onto the polymer backbone and thereafter subjecting or exposing the silane grafted polymer to water or atmospheric moisture. Preferably, the silane grafted polymer is subjected to or exposed to water or atmospheric moisture after a shaping or fabrication operation.

Suitable silanes for silane crosslinking of the polymer, e.g. the ethylene polymer, include those of the general formula



in which R^1 is a hydrogen atom or methyl group; x and y are 0 or 1 with the proviso that when x is 1, y is 1; n is an integer from 1 to 12 inclusive, preferably 1 to 4, and each R independently is a hydrolyzable organic group such as an alkoxy group having from 1 to 12 carbon atoms (e.g. methoxy, ethoxy, butoxy), aryloxy group (e.g. phenoxy), araloxy group (e.g. benzyloxy), aliphatic acyloxy group having from 1 to 12 carbon atoms (e.g. formyloxy, acetyloxy, propanoyloxy), amino or substituted amino groups (alkylamino, arylamino), or a lower alkyl group having 1 to 6 carbon atoms inclusive, with the proviso that not more than one of the three R groups is an alkyl.

Suitable silanes may be grafted to a suitable (ethylene) polymer by the use of a suitable quantity of organic peroxide, either before or during a shaping or fabrication operation. However, preferably, the silane is grafted onto the polymer before shaping or fabrication operations. In any case, the curing or crosslinking reaction takes place following the shaping or fabrication operation by reaction between the grafted silane groups and water. The water permeating into the bulk polymer from the atmosphere or from a water bath or "sauna". The phase of the process during which the crosslinks are created is

commonly referred to as the "cure phase" and the process itself is commonly referred to as "curing".

Any silane that will effectively graft to and crosslink the polymer can be used in the present invention. Suitable silanes include unsaturated silanes that comprise an
5 ethylenically unsaturated hydrocarbyl group, such as a vinyl, allyl, isopropenyl, butenyl, cyclohexenyl or γ -(meth)acryloxy allyl group, and a hydrolyzable group, such as, for example, a hydrocarbyloxy, hydrocarbonyloxy, or hydrocarbylamino group. Examples of hydrolyzable groups include methoxy, ethoxy, formyloxy, acetoxy, propionyloxy, and alkyl or arylamino groups. Preferred silanes are the unsaturated alkoxy silanes which can be
10 grafted onto the polymer. These silanes and their method of preparation are more fully described in US Patent No. 5,266,627 to Meverden, et al.. Vinyl trimethoxy silane, vinyl triethoxy silane, γ -(meth)acryloxy propyl trimethoxy silane and mixtures of these silanes are the preferred silane crosslinkers for use in this invention. If a filler is present, then preferably the crosslinker includes vinyl triethoxy silane.

15 The amount of silane crosslinker used in the present invention can vary widely depending several factors such as the silane itself, processing conditions, grafting efficiency, organic peroxide selection, the ultimate application, and similar factors. However, typically at least 0.5, preferably at least 0.7, parts per hundred resin (phr) is used. Considerations of convenience and economy are usually the two principal limitations on the maximum amount
20 of silane crosslinker used, and typically the maximum amount of silane crosslinker does not exceed 5, preferably it does not exceed 2, phr.

The silane crosslinker is grafted to the polymer by any conventional method, typically in the presence of a free radical initiator e.g. peroxides and azo compounds, or by ionizing radiation, etc. A suitable grafting method is disclosed in WO 95/29197, the disclosure of
25 which is incorporated herein by reference.

But, for efficient silane grafting, organic initiators are preferred, such as an azo compound or any one of the peroxide initiators, for example, dicumyl peroxide, di-tert-butyl peroxide, t-butyl perbenzoate, benzoyl peroxide, cumene hydroperoxide, t-butyl peroctoate, methyl ethyl ketone peroxide, 2,5-dimethyl-2,5-di(t-butyl peroxy)hexane, lauryl peroxide, and
30 tert-butyl peracetate. A suitable azo compound is azobisisobutyl nitrite. The amount of initiator can vary, but it is typically present in an amount of at least 0.04, preferably at least 0.06, phr. Typically, the initiator does not exceed 0.15, preferably it does not exceed about

0.10, phr. The ratio of silane crosslinker to initiator also can vary widely, but the typical crosslinker to initiator ratio is between 10 to 1 to 30 to 1, preferably between 18 to 1 and 24 to 1.

5 While any conventional method can be used to graft the silane crosslinker to the polymer, one preferred method is blending the two with the initiator in the first stage of a reactor extruder, such as a Buss kneader. The grafting conditions can vary, but the melt temperatures are typically between 160°C and 260°C, preferably between 190°C and 230°C, depending upon the residence time and the half life of the initiator.

10 Also suitable for the purpose of the present invention are moisture cure silane copolymers, such as ethylene-vinyl silane copolymers and ethylene vinyl acetate-vinyl silane polymers.

Crosslinking by irradiation may be accomplished by the use of high energy, ionizing electrons (electron beam), ultra violet rays, X-rays, gamma rays, beta particles, controlled thermal heating, or any combination thereof. Electron beam irradiation is preferred.

15 Advantageously, electrons are employed up to 70 megarads dosages. The irradiation source can be any apparatus known in the art such as an electron beam generator operating in a range of about 50 kilovolts to about 12 megavolts with a power output capable of supplying the desired dosage. The voltage of the electron beam generator can be adjusted to appropriate levels which may be, for example, 100,000, 300,000, 1,000,000 or 2,000,000 or

20 3,000,000 or 6,000,000 or higher or lower. In electron beam irradiation, the irradiation is usually carried out at a dosage between about 1 megarads to about 150 megarads, preferably between about 3 to about 50 megarads. Further, electron beam irradiation can be carried out conveniently at room temperature, although higher and lower temperatures, for example 0°C to about 60°C, may also be employed. Furthermore, electron beam irradiation

25 can be carried out in air atmosphere, or in reduced oxygen atmosphere or in inert gas atmosphere. Preferably, electron beam irradiation is carried out after shaping or fabrication of the article.

Also, in a preferred embodiment, a polyolefin is incorporated with a pro-rad additive and is subsequently irradiated with electron beam irradiation at about 8 to about 20

30 megarads. Suitable pro-rad additives are compounds which are not activated during normal fabrication or processing of the polymer, but are activated by the application of temperatures (heat) substantial above normal fabrication or processing temperatures or ionizing energy (or

both) to effectuate some measurable gelation or preferably, substantial crosslinking.

Representative pro-rad additives include, but are not limited to, azo compounds, organic peroxides and polyfunctional vinyl or allyl compounds such as, for example, triallyl cyanurate, triallyl isocyanurate, pentaerythritol tetramethacrylate, glutaraldehyde, ethylene glycol dimethacrylate, diallyl maleate, dipropargyl maleate, dipropargyl monoallyl cyanurate, dicumyl peroxide, di-tert-butyl peroxide, t-butyl perbenzoate, benzoyl peroxide, cumene hydroperoxide, t-butyl peroctoate, methyl ethyl ketone peroxide, 2,5-dimethyl-2,5-di(t-butyl peroxy)hexane, lauryl peroxide, tert-butyl peracetate, azobisisobutyl nitrite and the like and combination thereof. Preferred pro-rad additives for use in the present invention are compounds which have poly-functional (i.e. at least two) moieties such as C=C, C=N or C=O.

At least one pro-rad additive can be introduced to the polymer by any method known in the art. But, preferably the pro-rad additive(s) is introduced via a masterbatch concentrate comprising the same or different base resin as the polymer. Preferably, the pro-rad additive concentration for the masterbatch is relatively high e.g., about 25 weight percent (based on the total weight of the concentrate).

Pro-rad additives are introduced to the polyolefin in any effective amount. Preferably, the at least one pro-rad additive introduction amount is from about 0.001 to about 5 weight percent, more preferably from about 0.005 to about 2.5 weight percent and most preferably from about 0.015 to about 1 weight percent based on the total weight of the polymer. Crosslinking can also be promoted with a crosslinking catalyst, and any catalyst that will provide this function can be used. Suitable catalysts generally include organic bases, carboxylic acids, and organometallic compounds including organic titanates and complexes or carboxylates of lead, cobalt, iron, nickel, zinc and tin. Dibutyltindilaurate, dioctyltinmaleate, dibutyltindiacetate, dibutyltindioctoate, stannous acetate, stannous octoate, lead naphthenate, zinc caprylate, cobalt naphthenate; and the like. Tin carboxylate, especially dibutyltindilaurate and dioctyltinmaleate, are particularly effective for this invention. The catalyst (or mixture of catalysts) is present in a catalytic amount, typically between about 0.015 and about 0.035 phr.

The film, sheet, or coating of the invention may also comprise suitable mixtures, such as blends, of thermoplastic polymers. Polymer mixtures or compositions can be formed by any convenient method. If desired or required, compatibilization between two immiscible or

incompatible polymers can be effected by a suitable compatibilizer. Preparing the compositions by physical admixture includes dry blending, melt blending and solution blending, that is dissolving one or both of the components in a suitable solvent, such as for example a hydrocarbon, and combining the components followed by removing the solvent or solvents. Dry blending involves blending the individual components in solid particulate and subsequently melt mixing in a mixer or by mixing the components together directly in a mixer (for example, a Banbury mixer, a Haake mixer, a Brabender internal mixer, or a single or twin screw extruder including a compounding extruder and a side-arm extruder employed directly downstream of an interpolymerization process.

The mixtures can further be formed *in-situ*. For example, blends comprising a substantially linear ethylene interpolymer may be formed via interpolymerization of ethylene and the desired α -olefin using a constrained geometry catalyst in at least one reactor and a constrained geometry catalyst or a Ziegler-type catalyst in at least one other reactor. The reactors can be operated sequentially or in parallel. An exemplary *in-situ* interpolymerization process is disclosed in International Application WO 94/01052, incorporated herein by reference. The blends may be prepared using two reactors operated in series or in parallel, or by in-reactor blending using two or more catalysts in a single reactor or combinations of multiple catalysts and multiple reactors. The general principle of making polymer blends by in-reactor blending using two or more catalysts in a single reactor or combinations of multiple catalysts and multiple reactors is described in WO 93/13143, EP-A-0 619 827, and US Patent No. 3,914,362, each of which are incorporated herein by reference. The present polyolefin compositions can be prepared by selecting appropriate catalyst and process conditions with a view to the final composition characteristics.

Thermoplastic polymers suitable for use in the present invention also include recycled and scrap materials and diluent polymers (both encompassed by the expression "diluent materials"), to the extent that the desired performance properties are maintained. Exemplary diluent materials include, for example, elastomers, rubbers and anhydride modified polyethylenes (for example, polybutylene and maleic anhydride grafted LLDPE and HDPE) as well as high pressure polyethylenes such as, for example, low density polyethylene (LDPE), EAA interpolymers, ethylene/vinyl acetate (EVA) interpolymers and ethylene/methacrylate (EMA) interpolymers, and combinations thereof. In some instances, it is preferable for a polymer mixture to contain less than 50 weight percent, more preferably less than 30 weight percent diluent material, particularly when the diluent material is a

styrene copolymer, a styrene/butadiene rubber or a styrene/butadiene/styrene block copolymer (SBS).

Additives

Optionally, the film, sheet, or coating of the present invention may further comprise
5 additives, including, but not limited to, antioxidants (e.g., hindered phenolics, such as
IRGANOX™ 1010 or IRGANOX™ 1076 supplied by Ciba Specialty Chemicals), phosphites
(e.g., IRGAFOS™ 168 also supplied by Ciba Specialty Chemicals), cling additives (e.g.,
polyisobutylene (PIB), SANDOSTAB PEPQ™ (supplied e.g. by Ciba Specialty Chemicals),
pigments, colorants, deodorants, fillers, plasticizers, medical ornaments such as diaper rash
10 ornaments, UV stabilizers, heat stabilizers, processing aid and combinations thereof.

Although generally not required, the film, sheet, or coating of the present invention
may also contain additives to enhance antiblocking (antiblock agents) coefficient of friction
characteristics (slip agents) including, but not limited to, untreated and treated silicon
dioxide, talc, calcium carbonate, and clay, as well as primary, secondary and substituted
15 fatty acid amides, and combinations thereof.

Still other additives, such as quaternary ammonium compounds alone or in
combination with ethylene-acrylic acid (EAA) copolymers or other functional polymers, may
also be added to enhance the anti-static characteristics of the film, sheet, or coating of the
invention. Enhanced anti-static characteristics promote the usefulness of the inventive film,
20 sheet, or coating in, for example, cushioned packaging of electronically sensitive goods.

Films, Sheets, Coatings

The films, sheeting, or coatings used in and according to the present invention are
characterized in that they comprise at least one layer, which has a 'fringed' surface
microstructure. In this document, a film, sheet, or coating, or a layer thereof having such
25 fringed surface microstructure is also referred to as "fringed film, sheet, coating or layer",
including each item individually, e.g. "fringed film". The fringed surface microstructure may
cover a desired part or parts, or substantially the entire fringed item, depending on the
intended use of said item. When magnified, this fringed surface microstructure is shown to
be formed by a broken up base or matrix covered with fibrillar, strand-like or hair-like, spiky
30 aberrations. The base is seen to consist of a pattern of peaks or protrusions separated by
troughs or valleys. Irregularly shaped, fine tentacles or fibrils (herein referred to as 'fringes')
are protruding from these peaks. The fringes may be seen to have wave-like brims. A

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starting from a suitable precursor film, sheet, or coating. The structure of said precursor is characterized by a distinct surface texture consisting in a pattern of different (surface) thicknesses, i.e. areas of reduced thickness (valleys or troughs) and areas of greater thickness (peaks or protrusions). Advantageously, this pattern is predetermined and may be
5 irregular or regular.

Alternatively, the precursor may be a foamed structure, e.g. a film, sheet, or coating having a foamed surface layer. In such case, the precursor protrusions are formed by the microbubbles of the foam.

In the following, a film, sheet, or coating characterized by such pattern of different
10 surface thicknesses and suitable to give a fringed surface microstructure will be referred to as "precursor" (film, sheet, or coating). This includes a film, sheet, or coating which in part is characterized by such pattern of different surface thicknesses. The protrusions of the precursor surface are understood to be essential for the formation of the fringed surface microstructure in that such microstructure cannot readily be obtained from a regular smooth
15 film. For example, it was found that brushing of a smooth surface, e.g. of a basic film, sheet, or coating according to the techniques described hereinbelow does not result in the desired regularly fringed surface quality.

Advantageously, the height of the protrusions is at least about 20 microns, preferably at least about 50 microns and most preferably at least about 80 microns. The height of the
20 protrusions should be less than about 1 mm. Preferably, the height of the protrusions is in the range of from about 60 microns to about 500 microns, more preferably in the range of from about 80 microns to about 300 microns. Advantageously, the protrusions have a flattened or rounded top relative to the spiky ends of the fringes, edged structures are also suitable to form fringes. Preferred are protrusions in the form of knobs, naps, bumps or
25 truncated cones. Generally, the shape of the peaks or protrusions is affected by the viscosity of the thermoplastic polymeric material forming the peaks or protrusions.

To obtain the fringed surface microstructure the protrusions on the precursor surface are deformed such that they are essentially longitudinally and permanently extended. Deformation should be at least to, preferably beyond the yield point of the polymer forming
30 the protrusions. Preferably, such extension is the result of treatment using mechanical means. Advantageously and preferably, the fringes are obtained by stretching the protrusions by a factor of about two to about four. Stretching by a factor of below 2, e.g., by a factor of at least 1.1 may also provide the desired result. Stretching by a factor of e.g. 2

means that a protrusion which is 100 microns high is extended to a fringe length of 200 microns. As compared to the precursor, the fringed surface microstructure provides a substantially enlarged surface area.

For example, mechanical deformation suitable to create a fringed surface microstructure in accordance with the present invention may rely on the principle of friction and involve the use of an abrading device which has a harder surface or surface coating than the polymer surface to be treated. Suitable abrasives include, but are not limited to, sandpaper or sand-paper type materials, brushes, steel wool, or abrasive fabrics, such as a fleece or a non-woven having the required surface hardness. Suitable materials for the brush are, for example, nylon, glass-fiber or metal wire, such as bronze. It is readily apparent to the person skilled in the art that the number (density) and length of the fringes is affected by the type of abrasion material and the particular technique of treatment therewith. Critical parameters include deforming speed, applied pressure, temperature, particularly the polymer surface temperature, and hardness (difference). While any form of deformation movement may create a fringed surface microstructure, best results are obtained by circular, oscillating or linear movements, or any combination thereof. The general direction of these movements relative to the film surface and film orientation may be longitudinal, transverse, angled, or any combination thereof. If the treatment is essentially unidirectional, it is preferred to have at least two consecutive steps of either unidirectional or angled treatment. In the case of rotational or oscillating treatment, sequential treatment steps can improve the final quality of the surface. For each combination of surface hardnesses, i.e. surface hardness of the abrasion material and surface hardness of the polymer surface, exists an optimum type of movement and speed to obtain a particular fringed surface microstructure, e.g. fringe length and density. Such optimization is within routine experimentation. When magnified, e.g. using the SEM technique, the tops of the walls of the craters may be seen to be frayed, torn and elongated.

The mechanical treatment of the precursor may be performed in an in-line or an off-line process.

The precursor film, sheet, or coating may be produced using conventional methods. The precursor film may be uniaxially or biaxially oriented.

Generally, a film can be made by any known process including, but not limited to, solvent casting (for example, dispersion in a solvent, solvent including an aqueous medium

extrusion (for example, blown or casting), compression (for example, molding), roll milling or calendering, or any combination thereof. Extrusion as used herein is intended to include coextrusion, extrusion coating or any combination thereof. One or more films may be laminated to form a multilayer structure. The film may be oriented after forming using
5 known techniques and equipment, such as tenter frame, double bubble or trapped bubble orientation techniques. One or more layers of the film may be expanded, for example with a conventional blowing agent, to make a foamed film. To make foamed film structures or layers, either physical or chemical blowing agents may be used to achieve suitable foam densities, e.g. foam densities from 1 g/cc to as low as 0.01 g/cc. Suitable blowing agents
10 are known in the art. The foams may be open or closed cell, according to ASTM D2856. The cell sizes of the foams typically are from about 0.01 mm to about 5.0 mm, preferably from about 0.02 to about 2.0 mm. The foams may be crosslinked or non-crosslinked. As mentioned above, the fringed surface microstructure may be formed by mechanical treatment of a foamed surface.

15 A sheet can be made by any known process including, but not limited to, solvent casting, extrusion, roll milling, compression or calendering or any combination thereof.

A coating can be made according to methods known in the art, e.g. by extrusion coating or involving a roller and doctor blading.

For example, a process suitable for making a precursor film, sheet or coating may
20 comprise extruding a thermoplastic material in a molten state onto a moving belt or a roller surface which presents a negative or reverse structure with respect to the desired surface texture such that the thermoplastic material closely contacts said reverse structure. Advantageously, the surface temperature of the moving belt or roller is adjustable. The negative structure may, for example, consist of very fine cavities. Preferably, the process
25 conditions are such that the cavities are essentially completely filled by the thermoplastic material. This may be achieved by proper selection of the thermoplastic material, e.g. a polymer having a low viscosity, and/or proper selection of the temperature of the polymer mass, and/or by exposing the cavities to a vacuum such that the air is removed. Advantageously, the polymer mass filling the cavities is about at or above the Vicat softening
30 point. The thermoplastic material is solidified so as to adopt a surface texture which represents the positive counterpart of the negative structure of the moving belt or roller surface and thus form the desired precursor. After solidification, the precursor is removed from the roller or moving belt surface and subjected to further mechanical treatment suitable

to create the fringed surface microstructure, e.g. treatment as described above. A process suitable to prepare a precursor structure is disclosed in WO 97/02128, which is incorporated herein by reference.

5 A good fringed surface quality may also be obtained by allowing the molten polymer to fully solidify on the matrix roll during the surface shaping, meaning that more than about 90 % of the polymer is cooled well below the Vicat softening point. A compression molding process suitable to make the fringed surface structure used in the present invention is disclosed in WO 00/16965, which is incorporated herein by reference with respect to the process and devices described therein. Preferably, the process does not involve the
10 application of a vacuum.

Suitable equipment for such continuous compression molding process to make a fringed film, sheet, or coating comprises a set of surfaces, as presented for example by a pair of rollers, preferentially enabling temperature control, with defined surface qualities. The surfaces may have different, similar or equal surface roughness and shape. The surfaces
15 may be part of the primary equipment used to make the (base) film, sheet, or coating (in-line process), or be installed for a secondary compression molding process off-line. At least one surface, hereinafter referred to as matrix surface, is characterized by the presence of numerous cavities with a projected area of at least about 1000 square microns and a depth of at least about 100 microns. Such matrix surface structure can be provided by a porous
20 material, such as cast irons, an open cell, foamed material, by woven or entangled fibrous structures (e.g., natural, metallic, polymeric), by sintering of a suitable material, such as metallic, ceramic, polymeric or natural particles, or fibrous materials, by mechanical or chemical treatment of a suitable material, or by eroding techniques (electrical, chemical, lasering). Suitable techniques and technologies are known in the art. Such matrix surface is
25 applied on a device suitable for processing a film, sheet, or coating, such as a roller or a belt. Typically, the angle of the cavities relative to the matrix surface will be in the range of from about 45 to about 90 degrees.

To prepare the desired precursor having a pattern of different surface thicknesses a polymer mass, e.g. in the form of a polymer melt, polymer dispersion, polymer suspension,
30 polymer solution, film, sheet, or coating is applied on the matrix surface. Advantageously and preferably, the polymer mass is applied in form of a solid semi-finished product, in particular in form of a film, sheet, or coating. If desired, lamination (to that surface of the semi-finished product which is not facing the matrix surface) may be accomplished

simultaneously with the surface modification step. The mechanical properties of the semi-finished product will not essentially deteriorate or be substantially affected in the compression molding process.

One or more counter surfaces suitable to apply pressure onto the polymer mass, such as roller or belts, are used to force the polymer mass into the cavities of the matrix surface. Preferably, penetration of the polymer mass into the cavities is facilitated by heating the surface of the mass to a temperature which is at or above the Vicat softening point. The surface of the polymer mass is molded such that individual, distinct surface elevations or protrusions are formed in the cavities, thus yielding a suitable precursor structure. At the same time, the other surface of the polymer mass is shaped according to the structure of the counter surface of the pressuring device. The surfaces of the precursor reflect the surface characteristics of both rolls, the pressure roll and the matrix roll. Low viscosity of the polymer material filling the cavities is preferred.

After the surface molding, the film, sheet, or coating is released from the matrix surface which step requires sufficient web strength to pull the molded elevations out of the cavities. Sufficient web strength is achieved by appropriately cooling the precursor, if desired using additional external cooling sources, such as an air knife or cooling water. The fringe layer temperature and line speed should be adjusted to achieve minimal or no drawing of the polymer during removal from the matrix surface, and minimal to no adhesion to the cavity walls.

The tensile strength of the precursor may be enhanced by support layers. If the polymer mass fed into the compression molding equipment is a suspension or emulsion (additional) drying and/or curing and/or cross-linking may be performed on the matrix roller or belt, optionally in the presence of additional sources of energy for curing or crosslinking after the surface molding has occurred. Optionally, the fringed film, sheet, or coating thus obtained may be subjected to further mechanical treatment, e.g. with an abrasive device.

In order to avoid sticking of the film, sheet, or coating according to the invention to the equipment used in making said item or to facilitate release of the item, it may be desirable to use a sacrificial backing layer or protective layer. The sacrificial layer can be, but not limited to, oriented or non-oriented PET film, aluminum foil, non-woven/fleece, oriented or non-oriented polypropylene film, oriented or non-oriented polystyrene film, oriented or non-oriented PLA (polylactic acid) film, or natural fiber substrates, and/or a 'release aid',

such as PTFE, silicon, etc. as equipment coating materials (e.g. on the pressure roll or counter roll), or plasticizer or migratory additives in the polymer matrix (fatty acids, etc.). Film or sheet exhibiting a melting point which is at least 20°C higher than the fringed layer material are suitable as sacrificial layers.

5 Advantageously and preferably, the thermoplastic polymer or polymer blend forming the fringed surface microstructure is selected such that the fringes (after formation) are dimensionally stable, resilient and resistant to deformation under load at ambient temperature. Generally, polymer selection will be dictated by the particular process conditions for making the precursor and the fringed surface and the specific performance
10 requirements of the envisaged end-use applications. Optimal filling of the cavities with the polymer is favored by employing a thermoplastic having a low viscosity at the relevant processing temperature.

 Fringed films, sheets, or coatings, and articles of manufacture comprising such fringed film, sheet or coating particularly benefit from the fringed surface microstructure.
15 Performance attributes which can be specifically provided or enhanced by the fringed surface microstructure include soft, velvety and textile-like feel or touch, matte appearance, liquid repellency, anti-skid and good grip properties, surface variability and surface imprintability, controlled release properties, storage capabilities, and protective properties. Depending on the intended end-use application the fringed surface microstructure can be
20 designed and optimized to specifically exploit or favor one or more of these performance attributes, for example by selection of a proper polymer material or polymer materials, and/or of a proper fringe structure. If desired or required, the fringed film, sheet or coating may be made to provide additional functional properties, such as breathability, increased heat resistance, or barrier properties.

25 The present invention also relates to an article of manufacture made from or comprising a fringed film, sheet or coating. Based on the specific advantageous performance attributes afforded by the fringed surface microstructure such articles of manufacture are useful, for example, for decoration or as decorative materials, for packaging or as packaging material, for use as labels or signs, in automotive applications, for industrial, personal or
30 medical hygiene applications, for apparel or protective clothing, and for household applications.

More specifically, the fringed surface microstructure characterizing the articles of the invention can be designed to afford an excellent soft, velvety and textile-like feel or touch. The fringed film, sheet, or coating may show excellent haptics and be very pleasant and easy on a person's skin. Based on this property such fringed film, sheet, or coating is useful to manufacture plastic based articles used in soft touch, soft feel applications. For example, soft touch, soft feel materials are desirable in the automotive industry, for example on automotive interior surfaces, including but not limited to instrument panels, console liners, door panels, seat covers, headliners, and steering wheel covers. The fringed films, sheets, or coatings according to the invention are also useful to make decorative fabrics or articles with (direct) skin contact, for example, furniture covers including outdoor furnishing, such as desk covers, cushions, including patio air cushions, drapes, bedspreads, and table cloths; ostomy bags; mattresses including air mattresses; life vests; artificial leather (replacement); floor covering; medicinal and personal hygienic articles, including for example bandages, band aids, condoms, incontinence articles, such as diapers, or parts thereof including e.g., top sheet, ears or wings, cuffs, side panels, and back sheets; (disposable) garments apparel, and protective gear; such as medical drapes and gowns, athletic clothing, raincoats, hats and caps; grip bands; (bag) handles; linings, for example for luggage, bags or handbags, or shoes; gloves, and protective gear, artificial skin, skin imitations, toys, industrial hygienic articles, such as wipes or disposable toilet seat covers, head rest covers and the like. For end-use applications requiring a soft feel the fringe length is advantageously at least about 150 microns or more. Generally, use of polymers having a low modulus polymer will be advantageous to obtain a soft feel. The use of polymers having a higher modulus will result in differentiated haptics and tactility, affording a (relatively) rough feel rather than a soft feel. Articles with a fringe surface microstructure based on a polymeric material having a higher modulus can be useful, for example, as scouring or abrading devices, or to provide anti-skid performance.

Another benefit provided by the fringed surface microstructure is a matte (mat) appearance and further reduced gloss (relative to the precursor). Gloss is determined according to ASTM D-2457. The films, sheets, or coatings according to the invention are useful to manufacture articles relying on excellent aesthetics and matte optical appearance including, for example, decorative overlays, including wall, floor, or ceiling covering products; artificial flowers; linings of jewelry boxes and luggage; anti-glare surfaces such as billboards and window cling signs, merchandise bags, and projection and movie screens.

Another advantageous property characterizing the fringed film, sheet, or coating is a differentiated surface tension, as determined by the test methods according to ASTM D-2578 or DIN 53364, and water contact angle. The fringed films, sheets, or coatings are useful for applications and articles where surface water or liquid drain management, e.g. such that water beads up and drains off, is required. Such applications and articles include, for example, clothing with liquid repellant surfaces, e.g. rain gear, such as hats, coats, or ponchos, protective clothing, feminine hygiene top sheet, (disposable) table cloth and shower curtains.

Furthermore, the fringed surface microstructure also provides a frictional behavior, as reflected e.g. in the dynamic coefficient of friction, which affords anti-slip or anti-skid and better grip performance attributes to a fringed film, sheet, or coating, or an article of manufacture with a surface made from or comprising a fringed film, sheet, or coating of the invention. The dynamic coefficient of friction of a particular fringed surface may be determined according to ISO 8295, relative to various surfaces of interest, including, for example, the same or a different fringed surface, or a glass, metal, ceramic or polyolefin surface. The fringed surface microstructure provided herein typically provides an increased coefficient of friction as compared to non-fringed (plain) film of the same composition. The better grip and anti-slip properties make the fringed film, sheet, or coating useful for a variety of applications and articles including, but not limited to floor cover backings, furniture covers, gloves, table wear, bathroom articles, such as shower shoes and shower mats, roofing, tarps for construction, truck bed covers, box coatings, serving trays (e.g. as used in air planes or restaurants), grip bands or tapes, and non-skid operation room table cover.

The process for making gloves comprises dipping hand forms into a suitable dispersion, such as latex. The hand forms are cleaned, rinsed and dried. Subsequently, the forms are heated and a coagulant for the latex is added to support curing of the latex. The latex is applied to the forms by dipping the forms into the latex bath. Before the product is cured any undesirable solvents or materials are allowed to leach out during a leaching step. The gloves may be removed from the form by blasting them off by air, which is rather difficult to accomplish, or by peeling the latex off the form while inverting it at the same time. Prior to the curing or leaching steps, the gloves may be dipped into a bath for coating with another material. For example, the coating may serve to enhance grippage, increase the wearer's ability to hold onto slippery or wet instruments or improve the feel against a person's skin. The continuous compression molding process according to the present invention can

advantageously be used to make gloves with a fringed surface microstructure. In such process, the forms are employed as matrix surface. The peel/inversion process to remove the gloves from the form is applied such as to give the fringed surface microstructure. Thus the secondary dipping step of the conventional process becomes redundant.

5 Another benefit afforded by the fringed surface microstructure is surface variability, particularly surface printability or imprintability (embossing), as reflected in the possibility to create distinct areas of different topography, e.g. using suitable impression techniques. The fringed surface may be (im)printed with or without ink. Printability may be evaluated in terms of ink adhesion, color density (vividness), print definition employing suitable methods known
10 in the art, including for example adhesive tape peel tests, abrasion tests, or simply visual appearance. The ink may reside between the fringes as well as at the tips of the fringes. Acceptable ink adhesion is possible for water based and solvent based inks and should be selected based on the fringe layer polymer. Color density may vary dependent on the angle of view thus creating a unique 3D-type appearance. Clear fringed film may be reverse
15 printed, e.g. by printing the fringed microstructure and viewing from the reverse side.

Using, for example, a hot stamp, hot air or friction to re-melt and/or compress part of the fringes in a selected regular or irregular pattern to form a smooth surface, haptic and/or optic effects are achieved by the resulting difference in surface structure and appearance. Thus printing effects may be obtained without the need for color or ink. If the difference in
20 surface structure is marked, it may also be noticeable by a person with reduced visual ability or a blind person. Nevertheless, color or ink may be added to enhance the effects.

The desired imprinting effects may be realized relying on the same principles used in printing or sealing. For example, a stencil or print negative which is a metal or thermoset material that can be heated without distortion to temperatures above the melting point of the
25 thermoplastic polymer forming the fringes may be employed. Suitable temperatures for polyethylene are in the range of from about 50°C to about 200°C, preferably from about 60°C to about 160°C, more preferably from about 70°C to about 120°C. The image or pattern of the stencil or print negative is applied by pressing it on the fringed surface such that a three-dimensional effect is obtained. The effects are also obtainable in a process
30 which does not involve contacting the fringed surface, e.g. by applying a jet of hot effluent (e.g. air) similar to an air brushing printing process. Another process suitable to obtain imprinting effects is to abrade the fringes on the surface by a mechanical process and thus create areas of differentiated topography resulting in print-like images. Alternatively, to

obtain the described effects, the fringed surface may be created only on parts of the basic film, sheet, or coating 'a priori'.

The fringed surface microstructure can be printed with ink and resist ink from being scratched or abraded, thus enhancing the durability and appearance of the fringed article or item. The benefit of enhanced abrasion and scratch resistance is also afforded to coatings, such as barrier coatings, or metallization. By making the (barrier) coatings or deposits more scratch and abrasion resistant their particular properties will be maintained for a longer period of time. The advantage of improved scratch resistance also applies to printed or painted surfaces, e.g. in an automobile, such as dash boards, instrument panels etc., metallized films, e.g. used in the packaging of food, medical items or electronics, and barrier coated films.

Based on its surface variability and/or imprintability the fringed film, sheet, or coating of the present invention is particularly useful to make novelty balloons, book covers, wrapping paper, floor covering, ceiling covering or wall covering, labels, including, for example, in-mold labels and stretch labels, e.g. for bottles, bill boards, or paperboard coatings, e.g. for drinking cups, greeting cards, and party articles.

The increased surface area of the fringed film, sheet, or coating affords enhanced carrying, capturing or storing properties, which can be exploited for numerous applications and articles, including but not limited to articles comprising a controlled release system. For example, such system may provide for the controlled release of antibiotics and may be useful e.g. in wound covers or shower curtains, the controlled release of fragrances or the controlled release of drugs. Enhanced carrying, capturing or storage properties can also be exploited in wipes, tissues, carrier substrates for catalysis, filtration media, diaper top sheets, e.g. coated with diaper rash ointments, anti-static sheets, anti-fog films, and for HF weldability, thermal insulation, sound deadening, meat packaging and poultry diapers. The fringes are suitable structures, which other substances can be embedded into or coated onto. Such structures may allow, for example, the gradual diffusion or the controlled release of substances, such as drugs or fragrances. Such structures may be useful e.g. in transdermal drug delivery systems, fragrance delivery systems, such as soft packages for cosmetics or perfumes, or scented wall covering, or as filtration systems. A porous membrane may be put over the top of the structures to allow the soft surface to breath to the skin (drugs) or air (fragrances). If a barrier, for example made from SARAN™ or EVOH resin, is coated over the top of the reservoirs and the base of the film is made from a porous

material the drug is delivered through the base polymer. Emollients or salves can be placed between or on the fringes to maintain moistness for burn wounds or for diaper rash creams with the soft side against the skin. Antibacterial agents can be placed on the fringed surface to prevent mold and mildew formation, e.g. in shower curtains. Placing a static charge on the surface further enhances the ability to pick up substances, such as dirt or dust.

Furthermore, absorbent materials can be coated onto the fringed surface or be incorporated into the polymer (as a type of filler) before the fringed film, sheet, or coating is made, for example in order to enhance the absorption of coatings or ink. Examples of suitable absorbent fillers include, for example, superabsorbents used in hygiene applications, talc and calcium carbonate.

The fringed film, sheet, or coating may be made to be (moisture) vapor permeable or breathable. For example, breathable films include filled and stretched microporous films, or monolithic films, for example made from a thermoplastic polyurethane, a copolyesterether thermoplastic elastomer, a copolyesteramide thermoplastic elastomer or another highly water vapor transmitting polymer, such as a polyamide. A (thin) fringed layer may be coextruded on top of a previously stretched microporous layer or the fringed film can be stretched. A (thin) fringed layer can also be extruded on top of an inherently breathable monolithic layer. Water vapor breathability is a performance attribute desired or required for use of the fringed film, sheet, or coating of the invention in apparel, such as protective clothing, or in hygienic articles, such as (diaper) backsheet.

For example, a breathable monolithic fringed film is characterized by a high water vapor transmission rate (WVTR) and has a soft touch. In conventional breathable films, the soft touch has been provided by laminating a non-woven to the film. If desirable, the breathable monolithic fringed film may be laminated to another material which provides a different function in the composite, such as noise reduction or elastic recovery.

Advantageously, the fringed surface microstructure is designed so as to provide the desired water repellency performance or liquid impermeability. Thermoplastic polymers suitable to make (inherently) breathable fringed film include, for example, polyether block copolymer (e.g., PEBAX™ copolymer), and thermoplastic polyurethane (e.g., PELLETHANE™ polymer). The films may be mono-layer or multi-layer structures, preferably each layer having a high WVTR. The WVTR measured at 38°C and at 90% relative humidity (using ASTM method E96) should be in the range of 500 to 10,000 g/m²/day, more typically in the range of 1000 to 6500 g/m²/day. Such film is suitable for apparel or other applications for

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In a multi-layer structure, each layer will serve a particular function or provide some characteristic to the overall structure. The composition of these layers is chosen depending on the intended end use application, cost considerations, and the like.

For example, layers may serve to provide particular structural or functional characteristics, e.g. add bulk to the structure, promote interlayer adhesion, provide barrier properties, thermal properties, optic properties sealing characteristics, chemical resistance, mechanical properties, or abuse resistance. An adhesion promoting interlayer is also referred to as a tie layer. If a barrier layer is desired or required for the intended end use application, it is selected so as to meet the targeted degree of gas or moisture (im)permeability.

Various materials can be used for these layers, with some of them being used in one or more than one layer in the same film structure. Suitable materials include, for example, nylon, ethylene/vinyl alcohol (EVOH) copolymers, polyvinylidene chloride (PVDC), polyethylene terephthalate (PET), oriented polypropylene (OPP), ethylene/vinyl acetate (EVA) copolymers, ethylene/acrylic acid (EAA) copolymers, ethylene/methacrylic acid (EMAA) copolymers, LLDPE, HDPE, LDPE, graft adhesive polymers, such as maleic anhydride grafted polyethylene.

For example, a gas barrier layer may be made from vinylidene chloride copolymer, EVOH copolymer or SARAN™.

Examples of thermoplastic polymers appropriate for use in the seal layer include LLDPE, ULDPE, VLDPE, POP, EVA copolymer, EAA copolymer and ionomers.

Thermoplastic polymers for use in the bulk layer are advantageously chosen based on cost considerations and include recycled materials. Representative polymers are, for example, LLDPE, such as ethylene/butene copolymers, LDPE, EVA copolymer, (recycled) HDPE, polypropylene polymers and blends thereof.

Examples of thermoplastic polymers appropriate for use in a layer providing advantageous mechanical properties include, for example, ethylene/C₄-C₈ copolymers. The fringed multi-layer structures according to the invention typically consist of from two to seven layers. Preferred are multi-layer films having three or more layers.

Permeability may be provided by a porous membrane.

For example, it is within the scope of the present invention to provide a multi-layer film, sheet, or coating including the following general two-layer and three-layer structures, wherein the respective compositions of the layers are chosen from thermoplastic polymer resins which provide the requisite functional properties:

- 5 Fringed/Bulk
- Fringed/Seal
- Fringed/Adhesion
- Fringed/Bulk/Seal
- Fringed/Bulk/Adhesion
- 10 Fringed/Mechanical/Seal
- Fringed/Mechanical/Adhesion
- Permeability/Fringed/Barrier

For each of these general structures, further internal or external layers may be added to promote inner layer adhesion or add bulk, as appropriate.

- 15 The present invention also relates to the use of fringed film, sheet or coating in geomembranes.

- Furthermore, the present invention relates to the use of a fringed film in medical ostomy bags, urological collection bags and other liquid containment pouches. Furthermore, the invention relates to medicinal collection bags, such as ostomy bags, urological collection
- 20 bags and other liquid containment bags or pouches comprising a fringed film, particularly a multi-layer coextruded fringed film. The fringed surface microstructure is particularly advantageous and desirable for bags that are worn by a person and are in contact with his or her skin. Ostomy bags and urological collection leg bags are examples of patient-worn bags. In many commercial applications today, barrier films are combined with soft
- 25 nonwoven textiles, such as spunbonded or meltblown polyolefin or polyester nonwovens, to provide a laminate structure that can provide patient comfort when worn in contact with the body. The use of fringed film to impart soft "nonwoven" or textile-like feel to a coextruded barrier film structure can result in elimination of a separate nonwoven textile from a laminated bag structure.

- 30 Of particular interest for incorporation of a fringed film are coextruded barrier films that provide good oxygen, carbon dioxide and odor barrier properties. Barrier properties can be achieved by use of conventional barrier polymers such as polyvinylidene chloride (PVDC, such as SARAN® resin from The Dow Chemical Company), ethylene-vinyl alcohol (EVOH,

such as EVAL[®] resin from EVAL Company of America), nylon or amorphous nylon (such as GRILON[®] or GRILAMIDE[®] resin from EMS-Chemie, CAPRON[®] nylon from Allied Chemical or MXD6[®] nylon from Mitsubishi Gas Chemical Company), polyester (PET and PETG, such as EASTAR[®] polyester resins from Eastman Chemical Company) or phenoxy (such as BLOX[®] thermoplastic epoxy resins from The Dow Chemical Company). In
5 producing a coextruded barrier film, it is desired to provide outermost film layers that provide strength and sealability, such as with polyolefin resins. Suitable polyolefin resins include low density polyethylene (LDPE), linear low density polyethylene (LLDPE), high density polyethylene (HDPE), metallocene or plastomer polyethylene (mPE), ethylene-styrene
10 interpolymers (ESI), ethylene-vinyl acetate (EVA), ethylene methyl acrylate (EMA), ethylene-acrylic acid (EAA), and polypropylene homopolymer (PP) or polypropylene copolymer (coPP), chlorinated polyethylene (CPE), thermoplastic polyurethane (TPU), styrenic block copolymers such as styrene-butadiene-styrene (SBS) and styrene-ethylene-butylene-styrene (SEBS). These resins typically have poor affinity for and adhesion to the various barrier
15 resins, necessitating the use of suitable tie layer resins to bond the layers together. Tie layers may include polyolefin copolymers that are polar monomer modified, such as ethylene copolymers with 1 to about 40 weight percent of polar comonomer. Suitable ethylene copolymers include EVA, EMA, EAA, ethylene-n-butyl acrylate (EnBA), and maleic anhydride (MAH) grafted polyolefins such as PE-graft-MAH, PP-graft-MAH and EVA-graft-
20 MAH. These resins typically have 0.05 – 1.4 weight percent MAH grafted onto the polyolefin polymer.

Barrier films of the present invention are typically about 1.0 mils (25 μm) to about 10 mils (250 μm) in thickness, and preferably about 2.0 mils (50 μm) to about 6.0 mils (150 μm) in thickness. Thicknesses significantly greater than the preferred range can result in ostomy
25 bags or collection bags that are stiff and inflexible, resulting in poor conformation to a patient's body. This results in uncomfortable wearing of the bag, as well as aesthetically unacceptable bulging or protrusion of the bag from under the patient's clothing, eliminating the discreteness of wearing the appliance. In order to achieve good barrier properties, a typical barrier film will have a barrier layer of at least about 0.2 mils (5 μm) in thickness.

30 Suitable film structures include, for example, a symmetrical five-layer film with a core barrier layer, adjacent adhesive layers on either side of the barrier layer, and outermost skin layers on each side of the film. Such multi-layer structure can symbolically be represented as a "ABCBA" structure, wherein the "C" layer is a barrier layer, the "B" layers are adhesive

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It is additionally desired to utilize plastic tubing and/or plastic fittings or connectors on the film utilized for medical bags, pouches or appliances. These fittings and tubing are usually made of a material compatible with the film and bondable to the film. Tubing or fittings may be made of polyolefins such as polyethylene, EVA or EMA, or of TPU or flexible vinyl (PVC). Film structure and surface compositions may need to be formulated so as to provide suitable bonding via thermal welding, impulse sealing, high frequency (also known as radio frequency) sealing or mechanical fastening. Additionally, use of liquid curable adhesives or hot melt applied adhesives can be utilized to adhere tubing or fittings to a bag structure.

10 In yet another aspect, the present invention relates to a floor or wall covering product comprising a fringed film, sheet or coating according to the invention. In a preferred embodiment, the floor or wall covering is a multi-layer film or sheet comprising at least one layer having a fringed surface microstructure. The product may further comprise an optional print layer, an optional reinforcement layer and/or an optional foam backing layer. In a wall
15 covering product, the fringed layer may be present, for example, as the surface or top layer, the print layer or both. (Why not also the back layer, to store the glue?) In a floor covering product, the fringed layer may be the surface layer, the print layer and/or the backing layer, the fringed microstructure facing the floor. Used as a surface layer, the fringed microstructure is designed to afford soft touch and feel and may be imprinted, if desired. If
20 the fringed layer serves as a print layer, the fringed microstructure is designed to provide proper surface variability and imprintability. This layer is imprinted and preferably covered (on the top) by a transparent upper wear layer. As a backing layer the fringed layer affords anti-slip properties. If present, the reinforcement layer is an intermediate layer providing dimensional stability to the product, preferably a floor covering, which can be in excess of 4
25 meters in width. The optional intermediate reinforcement layer may be a melt processed polyolefin polymer or a non-woven or woven textile material. Preferably, the optionally intermediate reinforcement layer is a non-woven glass fleece material or a non-woven polymeric material. If present, the foam backing layer imparts resilient cushioning properties to the product and can also impart noise and thermal insulation characteristics to the product
30 as well as provide a barrier against microorganisms. Suitable resilient foam backing layers comprise or consist of a solvent dispersed polyolefin polymer, a melt processed polyolefin polymer or a latex composition. The product may further contain appropriate additives, e.g.

flame retardant additives to insure compliance with flame retardant requirements and other regulatory requirements.

Examples

5 The following Examples are illustrative of the invention, but are not to be construed as limiting the scope thereof in any manner. The following abbreviations are used: ESI = substantially random ethylene/styrene interpolymer; MFI or MI = melt flow index (measured at 2.16 kg/190°C according to ASTM D-1238, condition E); N/T = not tested; the pressures are indicated in MegaPascal (MPa) and the temperatures are in degree Celsius.

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Example 1: Three-layer coextruded precursor films

 A calender comprising two steel rolls is used to produce three-layer coextruded precursor films which are surface textured on one outer layer. The upper roll is electrically heated. The lower roll or matrix roll is coated with a crosslinked fluorelastomer, laser
15 microperforated and provides means for temperature control. The coating layer contains 2500 microholes per square centimeter. The holes are round and 200 microns long. An external heating device (hot air fan) to preheat the film surface is available and used as required. Variable parameters are: calender speed, roll temperature (film temperature), roll gap and roll pressure.

20 The three-layer coextruded film with an outer layer having a low Vicat softening point is pressed against the perforated roll to create a surface textured side with knobs of variable length (depending on the temperature of the perforating roll, film temperature and the pressure). Subsequently, the surface textured sides of these 'precursor films' are brushed or scrubbed in an off-line process to obtain fiber-like deformation and create a fringed film.

25 The three layer coextruded (basic) films used to prepare the precursor films have the following general structure:

 Outer layer/ Backing layer A/ Backing Layer B.

 In each of these films: the outer layer is made from a blend of 73% ENGAGE™ 8401 and 27% ENGAGE™ 8402 resins, both available from DuPont Dow Elastomers; backing layer A
30 serves to provide bulk and is made from LDPE resin, e.g. LDPE 300R available from The Dow Chemical Company; and backing layer B has a varying composition (and function), being made from:

- a) VLDPE or ULDPE resin, such as ATTANE™ SL 4101 available from The Dow Chemical Company
- b) HDPE
- c) Polypropylene
- 5 d) Ethylene Acrylic Acid Copolymer.

Each of the three layers may optionally further contain pigments, mineral fillers, plasticizer and/or migratory additives.

The three layer structures are 60 microns, 80 microns and 100 microns thick. In each structure, the outer layer makes up 60 percent of the overall thickness and the backing layers each make up 20 percent.

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Example 2: Three-layer fringed films

The outer layers of the precursor films of Example 1 are mechanically treated with the following devices:

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- Rectangular, flat phosphor bronze brush, filaments having a diameter of 0.2 and a length of 25 mm.
 - Rectangular, flat bronze brush, filaments having a diameter of 0.15 and a length of 20 mm.
 - Round bronze brush, round, filaments having a diameter of 0.15 and a length of 20 mm.

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 - Round glass fiber brush, filaments having a diameter of 0.2 and a length of 20 mm.
 - Round abrasive fabric (PET nonwoven impregnated)
 - Rectangular, flat abrasive fabric (PET nonwoven impregnated),
 - Sandpaper
 - Steel wool.

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The flat brushes are used to brush the film, stretched over a polyethylene cylinder (diameter of 5 cm) with unidirectional and circular movements in various film orientation directions. The round brushes are fixed on a conventional drill running at different speeds.

The abrasive fabric, sandpaper or steelwool is used in unidirectional and oscillating

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movements at various speeds. Best results with respect to regularity of the fringed surface and soft, velvety textile-like touch are obtained with oscillating or multidirectional movements using an abrasive fabric. The created fringes are up to 250 to 280 microns long.

If during formation of the precursor film the polymer is allowed to fully solidify on the matrix roll such that more than 90% of the polymer is cooled down well below the Vicat softening point of the polymer before the film is removed, a satisfactory fringed surface quality is achieved even without subsequent brushing or scrubbing.

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Example 3: One-layer fringed film comprising substantially random ethylene/styrene interpolymers (ESI)

The precursor film is made from a composition containing the following ingredients,
10 the numbers in brackets indicating weight percent:

ESI-1 Blend(50.6)

ESI-2 (36.8)

Polystyrene STYRON™ 648 (4.6)

Zinc Stearate ZnSt_2 (0.46)

15 Irganox B225 (0.18)

CaCO_3 (5.6)

TiO_2 Kronos 2220 (1.67)

Other additives (0.09).

ESI-1 Blend is a blend of ESI-1 (MFI: 1 g/10 min; copolymer styrene content: 30%;
20 atactic polystyrene: below 10 %) and HDPE IP 60 (MFI: 60 g/10 min, density: 0.952 g/cc) in a ratio of 75:25. The blend has a calculated MFI of 22 g/10 min and a calculated styrene content of 22 %. ESI-2 has a MFI of 1.0 and a styrene content of 69 %.

The monolayer basic film having a thickness of 70 microns is formed into a precursor film using the equipment described in Example 1 above. To prevent sticking of the film to the
25 (upper) steel roll, aluminum foil was placed between the ESI and the steel roll, the foil serving as sacrificial or protective backing layer which is subsequently removed from the precursor film. Brushing of the precursor film yields a fringed film having a soft, velvety and textile-like feel.

In general it is expected that all film or sheet substrates exhibiting a melting point of >
30 20°C compared to the fringe layer material or providing good release properties to molten polymers can be used as sacrificial layers. It is also expected that the same performance be achieved when such materials are coextruded with the fringe layer material.

Example 4: Fringed film comprising poly(lactide)

A three-layer co-extruded A/B/A cast film of the composition 15/70/15 Bionolle 1001 + 17% TiO₂/EcoPLA 4002/Bionolle 1001 + 17% TiO₂ is formed into a precursor film. EcoPLA 4002 is available from Cargill Dow and consists of poly(lactide) (12.5 % D isomer + 20% Citroflex A4 (acetyl tri-n-butyl citrate). Bionolle 1001 is an aliphatic polyester (polybutylene succinate) available from Showa High Polymer Co. Ltd.. Using the equipment and techniques described in Example 1, the basic film is formed into a precursor film which is subsequently brushed to give a fringed film having a soft, velvety touch.

Example 5: Water Repellency of Fringed Film

To examine the water repellency or water management characteristics of fringed film the water contact angle test is utilized. Testing is done according to ASTM D- 5946 utilizing method 1 in 3.1.2.1. In this test method water droplets are placed on the surface of a film sample, and the contact angle values are measured and then averaged. The contact angle is measured directly with a protractor by using tangential alignment of a cross-hair line to the point at which the side of the water droplet contacts the substrate. Water contact angle can then be related to wetting tension via a conversion chart. This test is used to compare the effect that the fringed surface microstructure has on the water repellency or the ability to enable the water to bead up on the surface.

It is found that the fringed film gives approximately 40 to 45 percent higher contact angle measurements as compared to non-textured films indicating that the fringed surface allows more water to bead up than the control. Such effect is important for applications requiring water repellency, such as raincoats and other water repellant outerwear, house wraps, feminine hygiene and diaper top sheets, and (latex) gloves (prevent formation of a slippery surface).

Example 6: Physical Properties

Tensile and tear properties are determined for a three-layer fringed film (layer ratios: 50% fringed/ 30% core/ 20% outside) of the following composition:

fringed layer: 6 wt.% slip masterbatch, 27 wt.% of a homogeneous ethylene/octene copolymer having a density of 0.885 g/ccm and a MFI of 30 g/min, 67 wt.% of a homogeneous ethylene/octene copolymer having a density of 0.902 g/ccm and a MFI of 30);
core layer: 87 wt.% LDPE 300R, 13 wt. % White Masterbatch;

A smooth (non-textured) base film of the corresponding structure and composition is used as control. Machine and cross direction tensile peak loads are determined according to the ASTM D-882 method, Elmendorf tear testing is performed according to ASTM D-1922.

Sample	Test	Cross Direction	Machine Direction
Control	Average Peak Load	9.7 lb/f	9.8 lb/f
Fringed	"	8.9 lb/f	11.0 lb/f
Control	Average Tensile Yield Load	5.6 lb/f	5.2 lb/f
Fringed	"	6.4 lb/f	5.9 lb/f
Control	Elmendorf Tear	667.2 g	206.4 g
Fringed	"	899.2 g	190.4 g

A composition consisting of the following components and amounts is gelated on a
10 roll mill and converted into a 100 micron film:

15 Using a compression molding process, solid fringes with a length of 120 microns are obtained.